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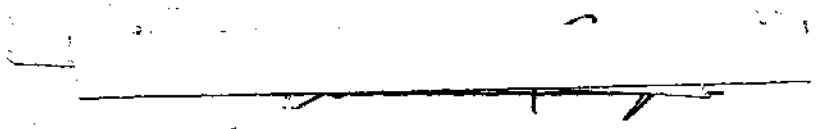

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CHEMICAL REACTION AND CHROMATOGRAPHIC SEPARATION IN A PACKED TUBULAR REACTOR

A THESIS

Presented to

The Faculty of the Graduate Division

by

C. Turner Lewis, Jr.

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CHEMICAL REACTION AND CHROMATOGRAPHIC SEPARATION

IN A PACKED TUBULAR REACTOR

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NOMENCLATURE

This table contains symbols which are used frequently throughout the investigation. Not included are common mathematical symbols or symbols which are both defined and used locally within the body of this work.

Symbol	Definition
A	molar concentration of component A, moles/l.
A_o	initial molar concentration of component A, moles/l.
B	molar concentration of component B, moles/l.
B_o	initial molar concentration of component B, moles/l.
C	molar concentration of component C, moles/l.
C_o	initial molar concentration of component C, moles/l.
D_i	effective diffusion coefficient of component i, $cm.^2/sec.$
D_i^o	reduced effective diffusion coefficient of component i, (D_i/R_oL).
g	half width of initial concentration square wave.
h	grid interval in X-direction.
i	reduced distance grid coordinate
j	reduced time grid coordinate.
k	grid interval in T-direction.
k_1	forward reaction rate constant, $(moles/l.)^{-1}(sec.)^{-1}$.
k_1^o	reduced forward reaction rate constant, $(moles/l.)^{-1}$.
k_2	reverse reaction rate constant, $(moles/l.)^{-1}(sec.)^{-1}$.

Symbol	Definition
k_2^o	reduced reverse reaction rate constant, $(\text{moles/l.})^{-1}$.
L	column length, cm.
R_i	column velocity of component i, cm./sec.
R_o	arbitrary constant, cm./sec.
R_i^o	reduced column velocity of component i, (R_i/R_o).
t	time, sec.
t_{Ri}	peak emergence time, of component i, sec.
T	reduced time, (tR_o/L).
T_R^o	reduced peak emergence time.
ΔT_i	extrapolated chromatogram peak basewidth, sec.
x	distance, cm.
X	reduced distance, (x/L).

SUMMARY

The amount of product formed in a reversible reaction is limited by the existing equilibrium. Some method of removing the product from the reaction mixture may be used to increase the yield of reversible reactions, thereby forcing the reaction substantially closer to complete conversion. Another method of driving to completion an equilibrium-limited reaction in which at least two products are formed would be the use of a combination tubular reactor-chromatographic unit, a so-called chromatographic reactor.

A chromatographic reactor is a tubular reactor which contains a packing capable of catalyzing the reaction and separating the products. This packing does not have to be a homogeneous material capable of both processes, but may be a heterogeneous packing consisting of a catalyst mixed with a material capable of separating the products. In the chromatographic reactor an inert carrier gas flows continuously through the packed column. Discrete reactant samples (or mixtures of the reactant and products) are introduced into the carrier gas at intervals sufficient to insure that no two samples occupy the same portion of the column at any time. If a difference exists in the rate of travel of the various products through the column, the products will separate and cannot react in the reverse direction to reduce the yield. In effect the reaction has been forced to an increased yield. Depending on physical considerations, almost any desired degree of completion can

result. This method has the added advantage of producing separated products and thus eliminating the usual purification step.

The objective of this investigation was to present a reasonable mathematical model of the chromatographic reactor with solutions which would enable prediction of the conditions required for a desired separation and conversion.

The simplifications used by previous authors to represent mathematically the chromatographic reactor and to subsequently solve the resulting equations have severely limited the usefulness of their solutions. Assumptions of instantaneous equilibrium, irreversible reactions, and zero diffusion prohibit their solutions from realistically representing any practical chromatographic reactor. None of the solutions can be used to quantitatively predict the conditions required for a desired reaction.

The consideration of the effects of diffusion, finite reaction rates, and a reversible reaction greatly complicates a chromatographic reactor model. In this investigation, these effects were included in the mathematical description of the reaction $2A \rightleftharpoons B + C$ occurring in a chromatographic reactor. The system of equations developed consists of three nonlinear partial differential equations with their associated initial and boundary conditions.

The solution of this mathematical system by numerical techniques has become practical with the advent of high speed computers. The nonlinear parabolic equations were transformed by implicit finite difference approximations into systems of nonlinear algebraic equations.

These nonlinear systems form tridiagonal matrices which can be solved efficiently using a reiterative technique to approximate the nonlinear terms. Systems of equations similar to those used in this work have been shown to be stable and convergent by earlier workers. A product material balance was used during the calculations to monitor the reaction. All calculations were programmed for a Burroughs B-5500 Information Processing System.

The numerical solutions were compared with available analytical solutions for the limiting case of no reaction. The comparisons have shown the computer program to be an accurate finite difference approximation scheme over the entire range of variables investigated in this study.

An activated alumina-ferric oxide column was developed capable of separating a H_2-HD-D_2 mixture. Experimental nonreactive data from this column were used for a comparison with the numerical solutions to the equations describing the chromatographic reactor model. The main difference between the experimental and numerical chromatograms was due to the fact that the experimental chromatogram did not have symmetrical peaks. The nonreactive data of this study and H_2-D_2 exchange reaction data in the literature were used to calculate numerical chromatograms of the $2HD \rightleftarrows H_2 + D_2$ reaction occurring in the chromatographic reactor.

Following the analytical and experimental comparisons, the numerical scheme was used to obtain solutions of equations describing the chromatographic reactor over a sufficiently wide range of variables

to include most practical situations. The product yield was studied as a function of product peak separation, effective diffusion coefficient, reaction rate constants, and equilibrium constant.

Calculations were made which proved that neglecting the effect of diffusion and finite reaction rate constants results in a model of the chromatographic reactor that is not realistic. Predictions based on such a model can only indicate trends. Also the assumption that reversible reactions proceed irreversibly in a chromatographic reactor gives excessive reactant conversions, especially for high reaction rate constants and low equilibrium constants.

This investigation showed that the major factor limiting conversion in a chromatographic reactor is the effective diffusion coefficients of the reactant and products. Reactant conversions significantly in excess of the static equilibrium values are possible using the chromatographic reactor with reversible reactions whose equilibrium constants are equal to or greater than 0.001.

An interesting result of this study is the indication that large chromatographic separations of components and large reaction rate constants are unnecessary and result in only marginal further reactant conversion over that possible with more moderate values.

It was found that an optimum order exists for the rate of travel of the various reaction components through the column. The reactant should have a column velocity intermediate between the velocities of the two products to insure maximum conversion. Another requirement for maximum reactant conversion is the use of highly concentrated, equilibrated mixtures of reactant and products.

The chromatographic reactor concept has been shown to be an effective and practical method of obtaining reactant conversions of reversible reactions significantly in excess of the maximum possible in a batch or continuous tubular reactor. It was also noted that under certain circumstances almost complete conversion is possible accompanied by fully separated products needing no further purification.

CHAPTER I

INTRODUCTION

Chromatographic Reactor Concept

Normally the amount of product formed in a reversible reaction is limited by the existing equilibrium. Some method of removing one of the products may be used to increase the yield of reactions in which at least two products are formed, thereby forcing the reaction substantially closer to complete conversion. Several investigators (1,2,3) have proposed driving an equilibrium-limited reaction to completion through use of a combination tubular reactor-chromatographic unit -- a so-called chromatographic reactor.

In the chromatographic reactor, as in elution chromatography, an inert carrier gas flows continuously through the packed column. Discrete reactant samples (or mixtures of the reactants and products) are introduced into the carrier gas at intervals sufficient to insure that no two samples occupy the same portion of the column at any time. If a difference exists in the rate of travel of the various products through the column, the products will separate and cannot react in the reverse direction to reduce the yield. In effect the reaction has been forced to an increased yield. Depending on physical considerations, almost any desired degree of completion can result. In addition, separated products are obtained eliminating the usual product purification step.

A requirement of the chromatographic reactor is that the column packing must catalyze the reaction and separate the products. However, a homogeneous packing capable of both processes is not required. Instead, a heterogeneous packing consisting of a catalyst mixed with a material capable of separating the products would accomplish the equivalent results. An exception exists when a gaseous catalyst can be supplied in the carrier gas thus requiring only that the packing separate the products.

Chromatographic Reactors

The chromatographic reactor concept has been tested experimentally by two groups (4,5,6) using the dehydrogenation of cyclohexane to benzene. Conversions 30 percent higher than those obtained under static equilibrium conditions were observed in both cases. With the most favorable conditions, even higher conversions were obtained.

Apparently other workers have encountered a chromatographic reactor reaction earlier without fully realizing or intentionally employing this concept. Thomas and Smith (7) passed mixtures of hydrogen and deuterium through a chromatographic column packed with palladium. While they were only partially successful in separating hydrogen and deuterium, some of their anomalous results can readily be explained by considering that the catalytic conversion to hydrogen deuteride occurred during separation.

Hall et al. (8) and Gaziev et al. (9) used the chromatographic reactor technique with the cracking of 2,3-dimethylbutane and the dehydrogenation of cyclohexane to benzene, respectively. However, no

attempt was made to induce or measure any product separation.

The yields of many other reactions may be improved by the use of a chromatographic reactor. The requirements for increased yields by this method are first, that there be at least two products, and second, that all reactants travel through the column without appreciable separation.* One possible example is the dehydrogenation of isopropyl alcohol to acetone which has been studied by Erofeev (10) over a copper-magnesium oxide catalyst.

Previous Mathematical Chromatographic Reactor Models

Solutions of the equations describing systems similar to a chromatographic reactor have been attempted to predict the conditions required for a desired separation or to explain observed results. It will be of value to review the pertinent literature.

Sedimentation - Electrophoresis Solution

Gilbert and Jenkins (11) have mathematically determined the effect on the schlieren pattern of a reversible reaction $A \rightleftharpoons B + C$ occurring during sedimentation or electrophoresis of a solution. Although the equations derived were applicable to a chromatographic reactor, the authors found it necessary to make several limiting assumptions. In effect, diffusion and finite reaction rates were neglected and the resulting equations were solved to obtain the concentra-

*This insures that the reaction can proceed in the desired direction. Although this may at first appear to limit the usefulness of a chromatographic reactor, a judicious choice of the many partitioning agents available could allow separation of the products without appreciable reactant separation.

tion distributions of A, B and C as a function of distance for large values of time. In addition the solutions obtained were for boundary conditions different from those describing the chromatographic reactor. The effects of diffusion and finite reaction rates definitely limit the conversion in a chromatographic reactor and should be included in any mathematical model. Therefore, the solutions of Gilbert and Jenkins were not useful in this study.

Reaction in a Series of Countercurrent Extractors

The effect of a reaction occurring during a series of extractions, such as on a Craig machine, has been examined by Bethune and Kegeles (12). Concentration distributions for components A, B and C were calculated as a function of the number of transfers for the simultaneous occurrence of the reaction $A \rightleftarrows B + C$. While not directly considering diffusion, the authors developed equations along lines similar to the plate theory of chromatography which effectively included diffusion. However, there are two reasons that restrict these results to only a qualitative description of the chromatographic reactor. First, instantaneous equilibrium between reacting species was assumed and, secondly, the calculations were made for only 100 theoretical transfers. Chromatographic columns contain the equivalent of several thousand theoretical transfers or plates. These results would require lengthy extension to adequately describe the chromatographic reactor.

Bethune and Kegeles showed that regardless of the transfer rate through the column assigned the complex A, the maximum concentration of the complex must lie between the maximum concentrations of B and C.

(The present investigation demonstrates that this remarkable feature applies only for reactions having large reaction rates.) Also it was noted that under these conditions it was possible for a component to have more than one concentration peak.

Solution of Equations for Chromatographic Reactor

Two groups have presented a mathematical model of the chromatographic reactor. While their simplifying assumptions permitted solution of the equations, it will be advantageous to extensively explore these assumptions and their limitations.

Roginskii, Yanovskii et al. Model. The first attempted mathematical description (4) of a chromatographic reactor used the assumption that reversible reactions occurring during chromatographic separation are irreversible. This assumption was made because the products were continuously separating and could not react in the reverse direction once separated. However, there is actually a considerable period during which the products overlap and can react reversibly to reduce the yield. One reason which probably led to the irreversible assumption was the necessity of neglecting diffusion in order to obtain a solution. The absence of diffusion would greatly shorten the time that the products overlap. The combination of a first order irreversible reaction $A \rightarrow B + C$ and negligible diffusion resulted in a first order linear partial differential equation easily solved analytically.

Roginskii et al. (4,13) included in their treatment the effect of finite adsorption and desorption on the catalyst surface. Roginskii and Rozental' (13) actually solved the case where the adsorption kine-

tics are of the same magnitude as the reaction kinetics. It was suggested that these results be used to calculate the rate constants for both adsorption and chemical reaction of the components. A method was outlined utilizing the percentage conversion at variable temperatures and carrier gas velocities to determine these constants.

Tables were calculated by Gaziev et al. (14) for determining the reaction rate constant of various irreversible reactions of the form $nA \rightarrow B + C +$ other products, assuming instantaneous adsorption equilibrium and zero diffusion. The input reactant pulse shape was shown to effect the yield of those reactions other than first order. These results were used to calculate the heat of adsorption, the activation energy, and the reaction rate constant for the dehydrogenation of cyclohexane to benzene.

Recently a more complete mathematical description of the chromatographic reactor has been attempted by Roginskii and Rozental' (15). Through the use of statistical theory they were able to include the effect of diffusion. However, the limiting assumption of a reversible reaction proceeding irreversibly was retained. The solutions offered are only for first order irreversible reactions.

E. M. Magee et al. Model. The reversible reaction $A \rightleftarrows B + C$ has been treated mathematically for a chromatographic reactor by Magee (16). Using a highly simplified model that neglected diffusion and finite reaction rates, the author was able to solve the special case of reactant A and product B moving at the same rate through the column. These assumptions led to a first order partial differential

equation which was solved on an analogue computer. Under these conditions Magee determined the effect of the equilibrium constant, the rate of product separation and reaction time on the product yield. As a result, limits were placed on the magnitude of product separation and equilibrium constant necessary for a chromatographic reactor. A product separation as small as 3.3×10^{-4} cm./sec. or an equilibrium constant of 2×10^{-7}, was suggested as a minimum requirement.

Matsen, Harding and Magee (5,6) have experimentally tested the results of Magee using the dehydrogenation reaction of cyclohexane to benzene. While experiencing higher yields than those obtained under static equilibrium conditions, the stoichiometry of the dehydrogenation reaction and the particular elution velocity did not allow a quantative comparison with the mathematical solutions of Magee.

The simplifications used by previous authors to represent mathematically the chromatographic reactor and to subsequently solve the resulting equations have been shown to severely limit the usefulness of their solutions. Assumptions of instantaneous equilibrium, irreversible reactions, and zero diffusion prohibit the solutions from realistically representing any practical chromatographic reactor. None of the solutions can be used to quantitatively predict the conditions required for a desired conversion.

Objective of the Theoretical Investigation

It was noted (5) that the maximum possible yields cannot be estimated until a solution to the equations describing a realistic model is obtained. The first objective of this investigation was to present a

reasonable mathematical model of the chromatographic reactor together with solutions so that prediction of the conditions required for a desired separation and conversion would be possible.

The previous review has demonstrated the importance of considering the effects of diffusion, finite reaction rates and a reversible reaction in any realistic model of the chromatographic reactor. Inclusion of these effects greatly complicates the mathematical equations yielding a nonlinear system of three simultaneous partial differential equations. This system must be approximated by a finite difference scheme and subsequently solved on a high speed digital computer using reiterative techniques.

The solutions are of a generalized nature enabling other investigators to readily determine the percentage conversion for their particular reaction and chromatographic reactor. Product yield was studied as a function of product peak separation, effective diffusion coefficient, reaction rate constants and equilibrium constant over a sufficient range to include most practical situations.

A comparison of experimental chromatographic reactor data with the numerical solutions to the equations describing the chromatographic reactor model would determine whether the numerical solutions adequately represent a physical chromatographic reactor. A possible reaction that could be used in a chromatographic reactor to supply experimental data is the reversible H_2-D_2 exchange reaction, $2HD \rightleftharpoons H_2 + D_2$.* This reac-

*The H_2-D_2 exchange reaction is actually much more complicated than this equation indicates. It is generally agreed that there is first a dissociation of H_2 and D_2 into atoms, followed by the formation of HD.

tion has only one reactant and no net change on reaction of the total number of moles. In addition, the physical properties of all three isotopic variations of hydrogen should be very similar.

Separation and Reaction of H_2, HD and D_2

There is extensive literature available on the chromatographic separation of H_2, HD and D_2 and several papers indicating a reasonable reaction of HD producing H_2 and D_2 at the conditions required for separation. The mathematical treatment would not include a volume change because there is no change in the total moles of reactants plus products for this reaction.

Separation and Analysis of the Hydrogen Isotopes.

Thomas and Smith (7) obtained the first partial resolution of hydrogen and deuterium using elution chromatography. A 43 foot column packed with palladium and maintained at 175° was used with an argon carrier gas. Because of the separation difficulties encountered over the range of conditions tried, there appears little chance for a satisfactory separation on a palladium column. However, this column is of definite interest in a $2HD \rightleftarrows H_2 + D_2$ test of the chromatographic reactor for two reasons. First, hydrogen isotopes adsorbed on palladium undergo a dissociation into atoms insuring the occurrence of reaction and separation without resorting to a heterogeneous column packing. Second, the palladium column operates at a temperature much higher than the low temperature necessary for other chromatographic separations. At the higher temperature, larger reaction rates will be available. It is possible that later investigations will overcome the separation problems.

All other separations of hydrogen isotopes have been based on differences in adsorptivities on solid adsorbents. These differences exist only at temperatures below 90° K. and the majority of experiments have been at 77° K. An excellent review on the separation and analysis of various forms of hydrogen has been recently published (17). Readers interested in an extensive literature development on these separations are referred to the review. Only the papers of direct concern to the present work are considered here.

With mixtures of hydrogen and deuterium there are actually five components; the ortho and para forms and the reaction product hydrogen deuteride. Chromatograms obtained using most low temperature adsorbents have overlapping peaks for orthohydrogen and hydrogen deuteride. In order to separate a mixture of H_2, HD and D_2 into its three components, some method of preventing the ortho-para separation in the chromatographic column was required. The ortho-para separation can be prevented by constantly equilibrating the ortho-para isomers during the chromatographic separation. This method has been proved by Klinkenberg (18) and Giddings (19) who have made theoretical studies of the reversible reaction $A \rightleftharpoons B$ occurring on a chromatographic column. Only one peak appeared on the chromatogram. This peak had a retention time between the two pure substances and was broader.

Smith and Hunt (20) packed a 21 foot column of activated alumina coated with chromium oxide to insure ortho-para equilibration. Using neon as a carrier gas at 77° K., they obtained the first successful resolution of hydrogen, hydrogen deuteride, and deuterium.

At the low temperature necessary for separation the only carrier gases available are hydrogen, neon, and helium. Hydrogen cannot be used in this chromatographic reactor test because it is one of the products. Neon, used by Smith and Hunt, is expensive and requires recycle equipment to reduce the carrier gas cost. Helium appears to be the only logical choice. The main disadvantages of helium are the small difference in thermal conductivity between hydrogen isotopes and helium and the anomalous thermal conductivity behavior of mixtures of these gases. If the exit gas stream is passed through a hot copper oxide furnace before entering the thermal conductivity detector, the oxides of the isotopes are formed. The detector is much more sensitive to the oxides than to the isotopes themselves.

Moore and Ward (21) used this detection method with helium carrier gas in the second successful separation of hydrogen, hydrogen deuteride, and deuterium. A 12 foot column at 77° K., packed with activated alumina coated with ferric oxide to promote equilibrium between ortho and para isomers of hydrogen, was employed. Partial deactivation with carbon dioxide improved the peak symmetry. Moore and Ward noted that extreme alumina activation at 480° also led to ortho-para equilibration. Venugopalan and Kutschke (22) have successfully applied this method to the separation and analysis of the hydrogen isotopes. On a six foot activated alumina column with helium carrier gas the isotopes were separated in 40 minutes with noticeable peak tailing.

Other workers have improved the column preparation method of

Moore and Ward. Notable papers on the optimum conditions are those of Shipman (23), King (24) and Botter et al. (25).

Most experimenters now using helium carrier gas use the copper oxide combustion furnace to amplify the exit chromatographic signal. Furnace temperatures from 416° to over 750° have been used. Several papers (21,22,23,26,27) are available on application of this technique.

While the vast amount of hydrogen isotope separation has been performed on alumina columns, other adsorbents should be equally effective. Botter et al. (25) and Kwan (28) have investigated several adsorbents. Results of these papers suggested the possibility of using Molecular Sieve 13X (manufactured by the Linde Division of Union Carbide), a synthetic calcium aluminum silicate having an open and well defined structure of molecular dimensions, treated with ferric oxide. Greater peak separations and resulting component resolution should be attained.

Hydrogen Exchange Reaction Catalysts.

Kinetics of the reaction $H_2 + D_2 \rightleftarrows 2HD$ have been studied over chromium oxide and nickel catalysts by Gould et al. (29). Apparent equilibrium constants were calculated as a function of time for a temperature range of -190° to 110°. At -190° for chromium oxide, the apparent equilibrium constant rose to 0.50 in two hours and equilibrium was obtained in 26 hours. Nickel catalyst kinetics were much slower, yielding an apparent equilibrium constant of 1.34 in 21 hours. For very large times, the value of the equilibrium constant at -190° was reported to be 2.2.

Kummer and Emmett (30) followed the H_2-D_2 exchange reaction at -195° over singly and doubly promoted iron catalysts. Reaction time for half conversion was 3-10 seconds for the singly promoted catalyst and about 100 minutes for the double promoted catalyst.

Objective of the Experimental Investigation

A second objective of this investigation was to test the predictions of the solutions to the equations describing the chromatographic reactor model against experimental data of this study and the H_2-D_2 exchange reaction data of Kummer and Emmett (30).

In this work, chromatographic columns were developed capable of resolving H_2-HD-D_2 mixtures in a helium carrier. The columns were used to test the effectiveness of various catalysts held first at room temperature and later at 77° K. The extremely active, singly-promoted iron catalyst of Kummer and Emmett was tested along with other chromium oxide and nickel catalysts. Necessary calculations of the equilibrium molar concentrations at various temperatures were made using the tabulated data of Woolley et al. (31). The results of these tests were used to supply chromatographic reactor data. The experimental data were compared to the solutions of the chromatographic reactor model to determine if the developed model was realistic.

CHAPTER II

MATHEMATICAL DESCRIPTION AND SOLUTION

Mathematical equations describing chromatographic models are available (32,33,34) whose solutions are capable of realistically representing the separation of a nonreactive mixture of A + B + C. Extension of these equations for the reaction $2A \rightleftharpoons B + C$ in a chromatographic reactor is accomplished in this investigation.

The solutions presented here and in the previously mentioned papers are all based on a linear, nonideal chromatographic model which assumes that the equilibrium concentrations between the two phases are proportional (a linear adsorption isotherm), but includes the effects of finite mass transfer rates between the phases, diffusion, and other band spreading processes. Most gas-liquid chromatography can be adequately represented by these assumptions. Implicit in the use of a linear adsorption isotherm is that the calculated concentration distribution in the column will be symmetrical about its maximum concentration. The resulting chromatogram will be essentially symmetrical. If the experimental chromatogram for a nonreactive system is not symmetrical, the calculated results will not exactly represent the physical case.

The presence of asymmetrical chromatogram peaks does not necessarily imply nonlinear isotherms, only that the chosen chromatographic model yields non-symmetrical peaks only with nonlinear isotherms.

Other mechanisms, not included in the model, might have caused the actual asymmetry.

Mathematical Description of Model

Consider the component, A, moving with a velocity R_a cm./sec. through a packed column extending to infinity in both directions. Let the component enter the experimental section at x = 0 and leave at x = L. If the effective diffusion coefficient for component A is D_a cm.^{2}/sec., the change in concentration of A in the column (described as a function of time and distance) is

$$\frac{\partial A}{\partial t} = D_a \frac{\partial^2 A}{\partial x^2} - R_a \frac{\partial A}{\partial x} \tag{1}$$

With the addition of the reaction $2A \rightleftarrows B + C$, Equation (1) becomes

$$\frac{\partial A}{\partial t} = D_a \frac{\partial^2 A}{\partial x^2} - R_a \frac{\partial A}{\partial x} - 2k_1 A^2 + 2k_2 BC \tag{2}$$

where k_1 and k_2 are the forward and reverse reaction rate constants, respectively.

Similar equations can be written for components B and C.

$$\frac{\partial B}{\partial t} = D_b \frac{\partial^2 B}{\partial x^2} - R_b \frac{\partial B}{\partial x} + k_1 A^2 - k_2 BC \tag{3}$$

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2} - R_c \frac{\partial C}{\partial x} + k_1 A^2 - k_2 BC \tag{4}$$

Changing the two independent real variables x and t by the arbitrary relations,

$$T = t \left(\frac{R_o}{L}\right) \text{ and } X = \frac{x}{L}$$

and substituting the following reduced constants,

$$D_i^o = D_i/R_o L$$

$$R_i^o = R_i/R_o$$

$$k_1^o = k_1 L/R_o$$

$$k_2^o = k_2 L/R_o$$

the following equations result:

$$\frac{\partial A}{\partial T} = D_a^o \frac{\partial^2 A}{\partial X^2} - R_a^o \frac{\partial A}{\partial X} - 2k_1^o A^2 + 2k_2^o BC \tag{5}$$

$$\frac{\partial B}{\partial T} = D_b^o \frac{\partial^2 B}{\partial X^2} - R_b^o \frac{\partial B}{\partial X} + k_1^o A^2 - k_2^o BC \tag{6}$$

$$\frac{\partial C}{\partial T} = D_c^o \frac{\partial^2 C}{\partial X^2} - R_c^o \frac{\partial C}{\partial X} + k_1^o A^2 - k_2^o BC \tag{7}$$

R_o is an arbitrary constant with the dimensions of velocity and may be, for example, the carrier gas velocity or the column velocity of one component.

The initial conditions are:

$$A\ (X,0) = F_1\ (X)$$

$$B\ (X,0) = F_2\ (X)$$

$$C\ (X,0) = F_3\ (X)$$

with the boundary conditions, as X approaches plus and minus infinity,

$$A\ (X,T) = B\ (X,T) = C\ (X,T) = 0$$

An overall material balance gives,

$$\int_{-\infty}^{\infty} A\ (X,T)\ dX + \int_{-\infty}^{\infty} B\ (X,T)\ dX + \int_{-\infty}^{\infty} C\ (X,T)\ dX = \text{constant}$$

These three nonlinear, second-order partial differential equations with the associated boundary and initial conditions constitute the mathematical description of the chromatographic reactor model. While the material balance cannot be used to eliminate one of the equations, it serves as a useful check on the required mass conservation.

For this investigation the following initial conditions were used:

$$A(X,0) = A_o, \qquad -g < X < g$$

$$B(X,0) = B_o, \qquad -g < X < g$$

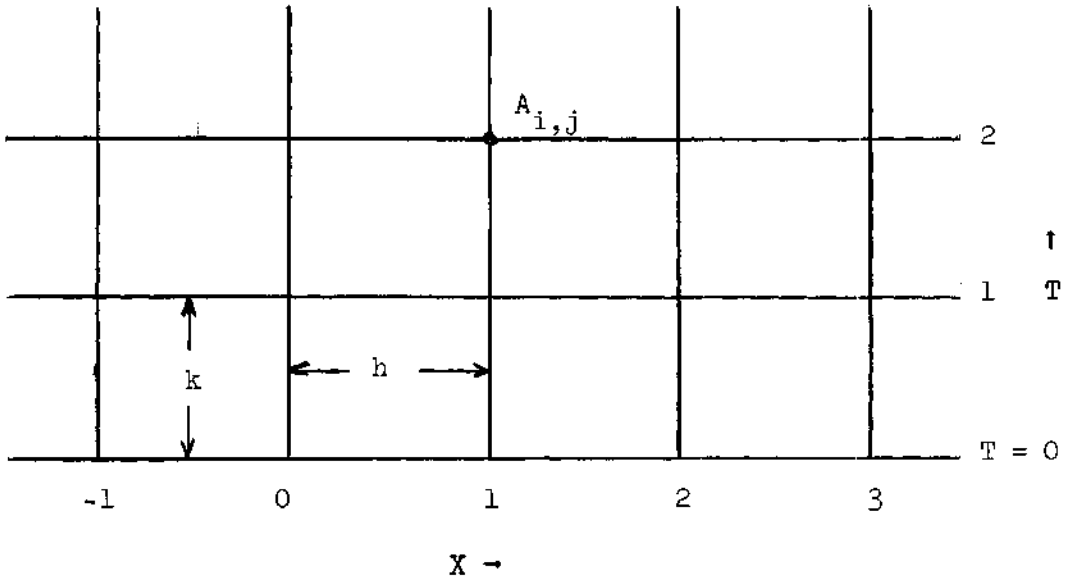
$$C(X,0) = C_o, \qquad -g < X < g$$

and

$$A(X,0) = B(X,0) = C(X,0) = 0, \qquad |X| > g$$

Outline of Numerical Solution

A rectangular semi-infinite grid is superimposed on the plane surface representing the X-T domain. This surface extends unbounded in the T-direction from time T = 0 and is sufficiently wide with respect to X to include the region of interest.



The rectangular grid is arranged with an h-interval in the X direction and a k-interval in the T direction. The set of points in the X,T-plane is given by X = ih and T = jk, where i and j are integers and j is restricted to non-negatives. If the number of internal points between X = 0 and X = 1.0 is called N, then it follows that

$$(N + 1)h = 1.0$$

Also the mesh point $A_{i,j}$ is equivalent to

$$A_{i,j} = A(X_i,T_j) = A(ih,jk)$$

If the functions A(X,T), B(X,T) and C(X,T) are considered point functions and implicit finite difference approximations substituted for the derivatives in Equations (5), (6) and (7), there results a quasi-linear algebraic system of equations for each dependent variable. Quasi-linear notation is used because some of the resulting matrix

coefficients are not constants, but depend on the local values of the dependent variables.

The resulting systems of equations form tridiagonal matrices which can be solved efficiently using the method of Thomas outlined by Bruce et al. (35). The nonconstant matrix coefficients complicate the solution, requiring a reiterative technique. Solutions based on estimated coefficients are obtained, followed by reiterations with the new solutions until the coefficient estimation error is within prescribed limits.

Detailed development of the finite difference equations and a description of the calculation scheme for the resulting matrices is given in Appendix A.

The computer program used for the above calculation scheme is described in Appendix B. Sample calculations are included in Appendix C.

Limiting Analytical Solutions

For the limiting case of no reaction, equation (5) reduces to

$$\frac{\partial A}{\partial T} = D_a^o \frac{\partial^2 A}{\partial X^2} - R_a^o \frac{\partial A}{\partial X} \tag{8}$$

Transforming the variable A from a function of X and T to a function of Z and T gives

$$\frac{\partial A}{\partial T} = D_a^o \left(\frac{\partial^2 A}{\partial Z^2}\right) \tag{9}$$

where $Z = X - R_a^o T$. This substitution is equivalent to using an X-axis moving at a constant rate, R_a^o.

If the initial concentration distribution of A in the infinite system is given by

$$A(Z,0) = A_o, \quad -g < Z < g$$

and

$$A(Z,0) = 0, \quad |Z| > g$$

then the solution is

$$A(Z,T) = \frac{A_o}{2}\left[\operatorname{erf}\left(\frac{g+Z}{2\sqrt{D_a^o T}}\right) + \operatorname{erf}\left(\frac{g-Z}{2\sqrt{D_a^o T}}\right)\right] \qquad (10)$$

The numerical solutions of the computer program were compared with the limiting analytical solutions for reduced effective diffusion coefficients of 0.002, 0.001 and 0.0005 at reduced times, T of 0.10, 0.40 and 1.00. The results have been plotted in Figures 1, 2 and 3 for A_o = 10.0 moles/l., R_a^o = 1.0, and g = 0.0025. These variables were selected as representative of the entire range used in this study.

It is evident that the numerical solutions coincide with the analytical solutions except for values of $D_i^o T \leq 2 \times 10^{-4}$. For the extreme case with the smallest reduced effective diffusion coefficient and the smallest reduced time, the numerical solution is only slightly skewed.

A common method of calculating the theoretical number of plates (which is related to the effective diffusion coefficient) is based on the assumption that the exit concentration chromatogram approximates a Gaussian shape. It can be shown that Gaussian curves exhibit band

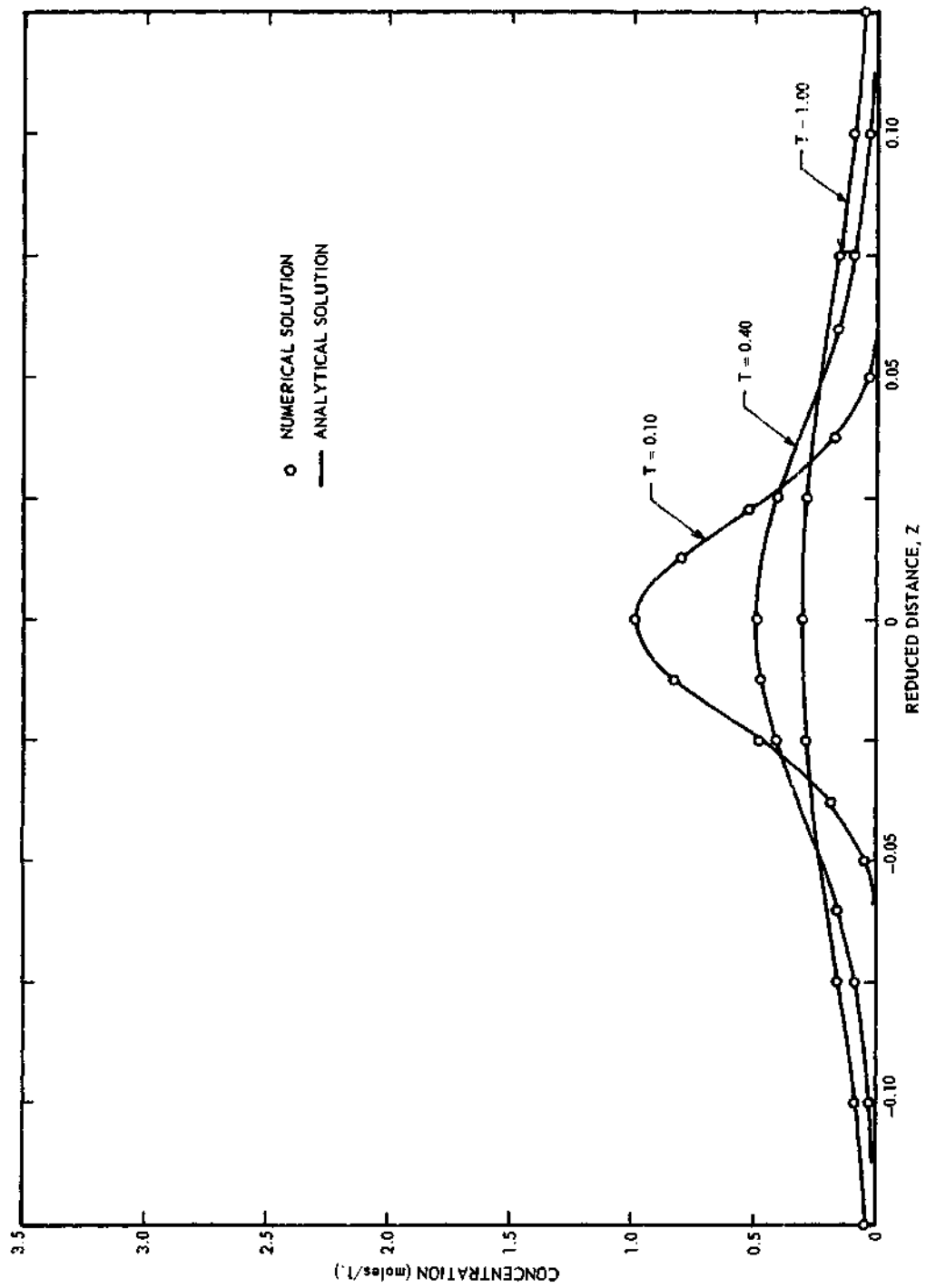


Figure 1. Comparison of Numerical and Analytical Solutions for No Reaction.
Initial Molar Concentration: 10.0 moles/l.
Reduced Effective Diffusion Coefficient: 0.002.
Reduced Component Velocity, R_a^o: 1.00.

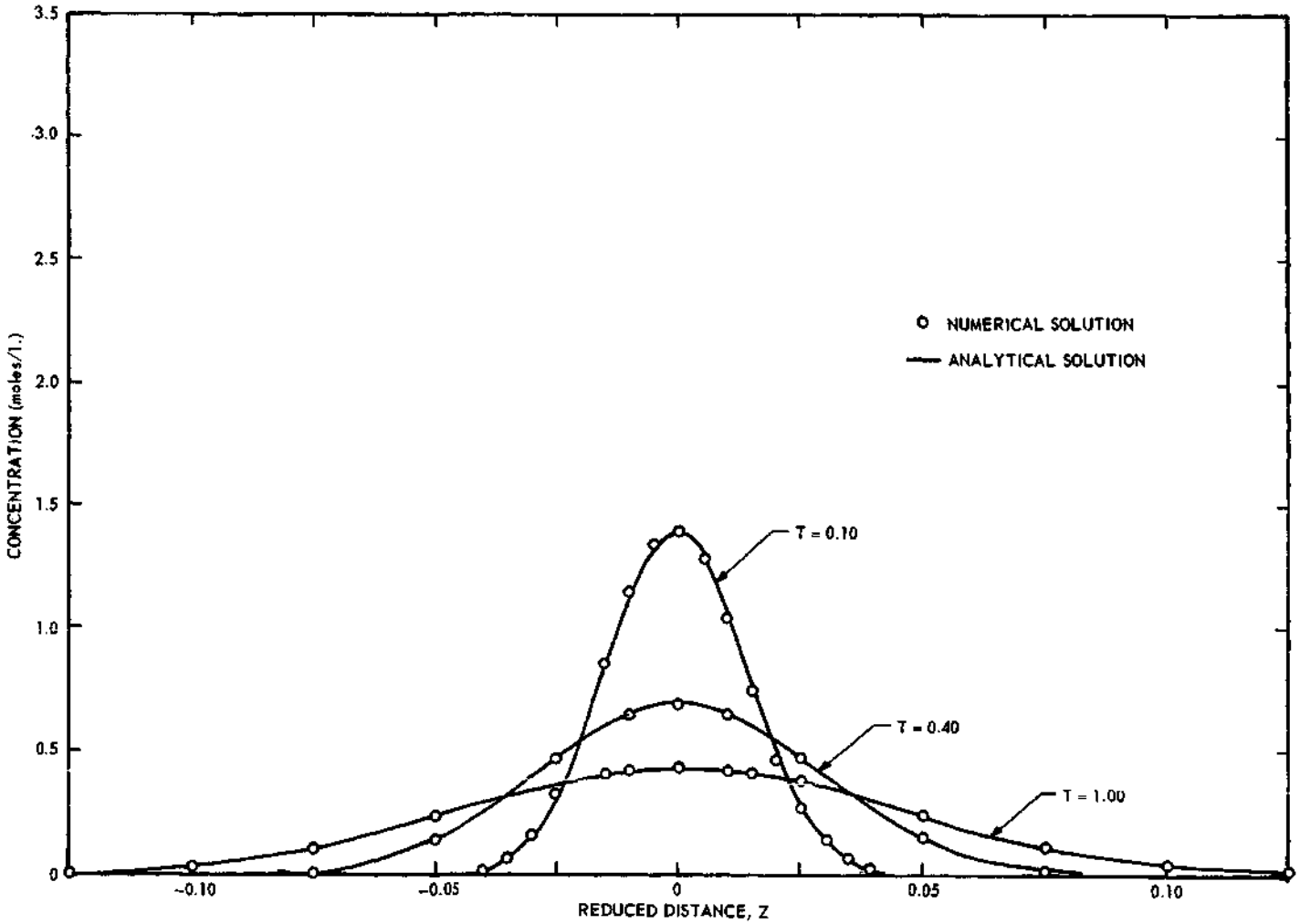


Figure 2. Comparison of Numerical and Analytical Solutions for No Reaction.
Initial Molar Concentration: 10.0 moles/l.
Reduced Effective Diffusion Coefficient: 0.001.
Reduced Component Velocity, R_a^o: 1.00.

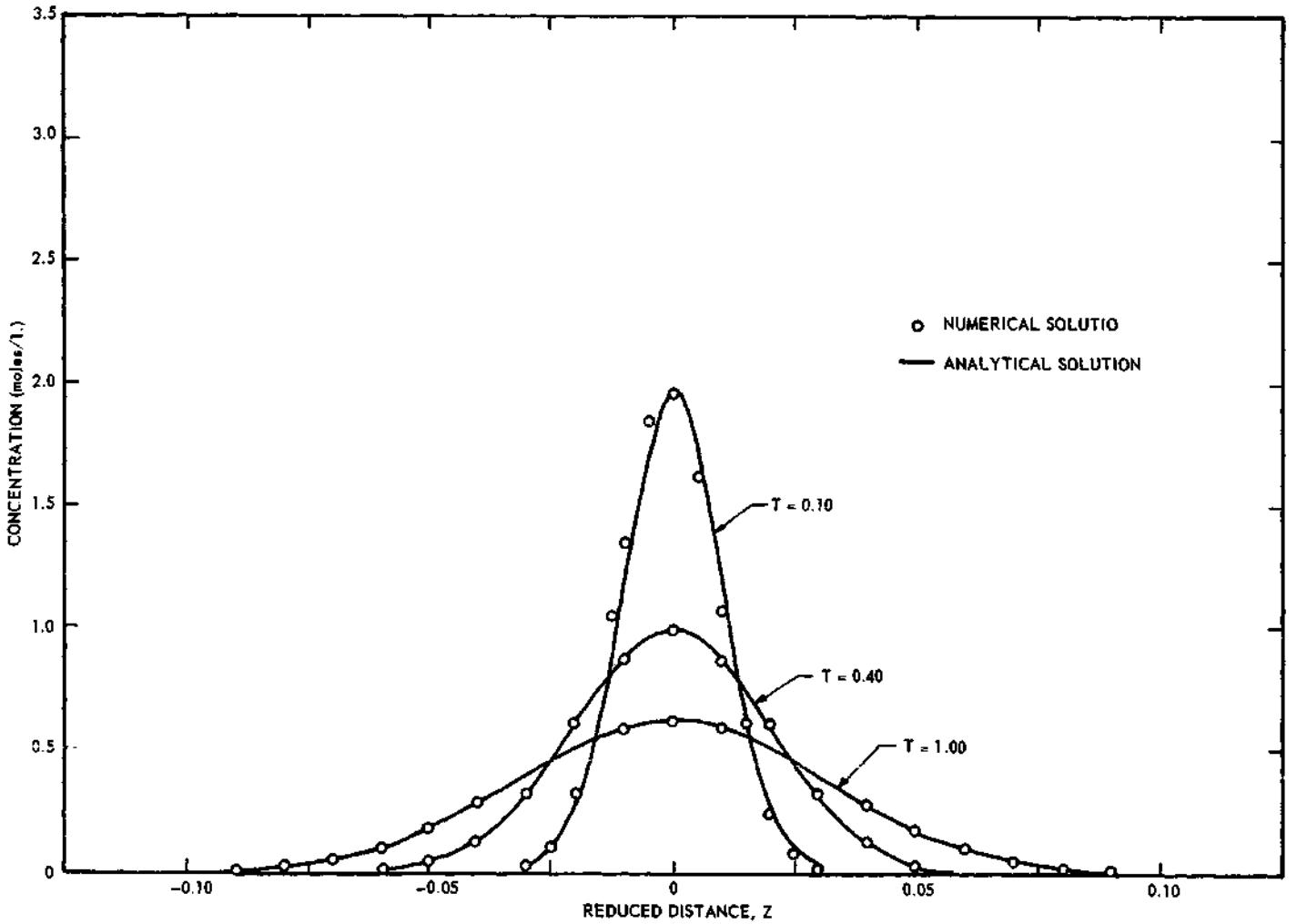


Figure 3. Comparison of Numerical and Analytical Solutions for No Reaction.
Initial Molar Concentration: 10.0 moles/l.
Reduced Effective Diffusion Coefficient: 0.0005.
Reduced Component Velocity, R_a^o: 1.00.

spreading proportional to $(DT)^{\frac{1}{2}}$. The peak basewidth (extrapolated by tangents through the inflexion points) is four standard deviations, 4σ. Rearranging the Einstein equation for diffusional spreading gives

$$D_i^o = \frac{\sigma^2}{2T_i}$$

where σ is measured in dimensionless length units. Converting σ to dimensionless time units (see Appendix C) yields

$$D_i^o = \frac{(\Delta T_i)^2 \ (R_i^o)^2}{32 \ T_i} \qquad (11)$$

where ΔT_i is the reduced extrapolated basewidth on the chromatogram, T_i is the reduced peak maximum emergence time, and R_i^o is the reduced component column velocity.

The concentration at the column exit ($X = 1.0$) was recorded during all numerical solutions. These computed chromatograms were used to calculate the reduced effective diffusion coefficients from the resulting peaks for an additional check of the computer program.

Using Equation (11), the calculated reduced effective diffusion coefficients agree with the coefficients supplied to the program within three percent. Graphs of the exit chromatograms for no reaction and reduced effective diffusion coefficients of 0.0005, 0.001 and 0.002 are given in Figure 4.

Analytical comparisons with numerical solutions have shown the computer program to be an accurate finite difference approximation scheme over the entire range of variables presently investigated for the limiting case of no reaction. Additional comments on the solution's mathematical stability and convergence are included in Appendix A.

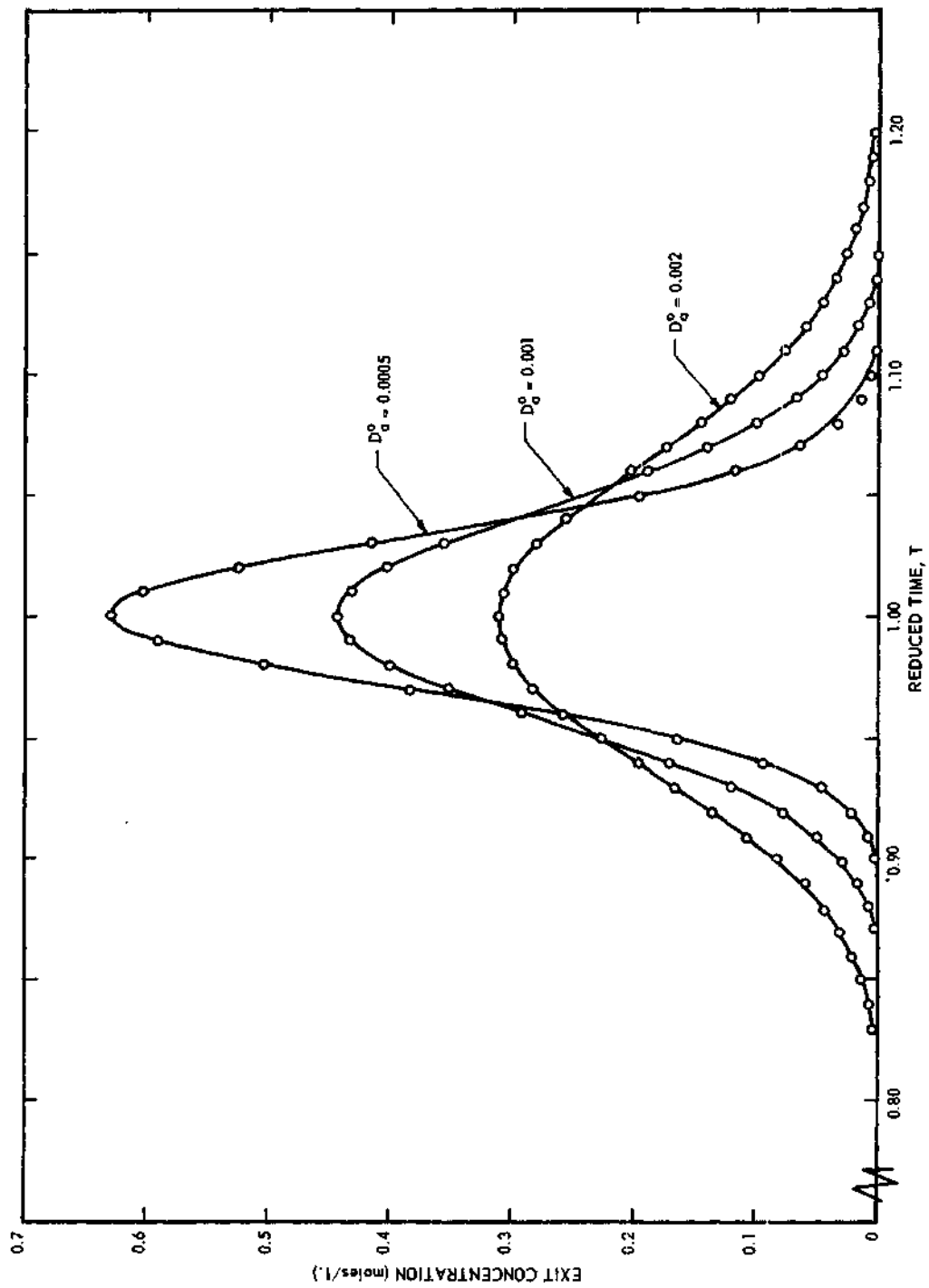


Figure 4. Exit Chromatogram of Numerical Solution for No Reaction.
Initial Molar Concentration: ^{o}10.0 moles/l.
Reduced Component Velocity, R^o_a: 1.00.

CHAPTER III

EXPERIMENTAL RESULTS

A comparison of experimental chromatographic reactor data with the numerical solutions of the equations describing the chromatographic reactor would determine whether the calculated results adequately represent the performance of a physical chromatographic reactor. One possible reaction that could be used in a chromatographic reactor to supply experimental data is the reversible reaction, $2HD \rightleftarrows H_2 + D_2$. There is extensive literature available on the chromatographic separation of H_2, HD and D_2 and several papers indicating a reasonable reaction of HD producing H_2 and D_2 at the conditions required for separation.

A requirement of the chromatographic reactor is that the column packing must catalyze the reaction and separate the products. A heterogeneous packing consisting of a catalyst mixed with a material capable of separating the products would be equivalent to a homogeneous packing capable of both processes. To provide a chromatographic separator tests were performed to determine the best adsorbent for the separation of H_2, HD and D_2. Subsequent tests were made of the ability of various catalysts to promote the H_2-D_2 exchange reaction in order to find the necessary catalyst for the heterogeneous packing.

Chromatographic Column Selection

The previous review of the separation of hydrogen isotopes

discussed several solid adsorbents that could be used to separate H_2, HD and D_2 at 77° K. without an accompanying ortho-para separation. These adsorbents are highly activated alumina, Molecular Sieve 13X treated with ferric oxide to promote equilibrium between the ortho and para isomers of hydrogen, and similarly treated, activated alumina.

Equipment

All chromatographic separations were performed on a Perkin-Elmer Model 820 chromatograph using Matheson high purity helium (minimum purity 99.995 percent) as a carrier gas. Before entering the chromatograph the helium was passed through a Molecular Sieve 5A column to remove the last traces of moisture and other impurities.

The Perkin-Elmer Model 820 chromatograph has as standard equipment a hot wire thermal conductivity detector especially designed to obtain the maximum possible sensitivity using chromatographic columns with an outside diameter of one-eighth inch. All the columns tested were made from one-eighth inch refrigeration grade copper tubing. This size of tubing permitted construction of extremely compact columns. In addition, only relatively small amounts of adsorbents were required to fill the columns.

Modification of the chromatograph was necessary to allow column operation at 77° K. Each column tested was placed in a Dewar flask filled with liquid nitrogen. Short connections were made to the chromatograph with copper tubing packed with 80-100 mesh glass beads to insure a flat velocity profile.

Sample injection was accomplished, using Hamilton gas-tight

syringes or the gas sampling valve supplied with the chromatograph.

Mixtures of H_2, HD and D_2 were prepared by equilibrating H_2 and D_2 over a hot filament at approximately 1000° K. for 20 minutes. (At 1000° K. an equal molar mixture of H_2 and D_2 react to yield an equilibrium HD mole fraction of 0.497 (31).) For all sample preparations Matheson c.p. grade deuterium (minimum purity 99.5 percent) and Matheson prepurified grade hydrogen (minimum purity 99.95 percent) were used.

A Sargent Model SR potentiometric recorder with a one millivolt full-scale sensitivity was connected to the bridge output of the thermal conductivity detector.

Highly-Activated Alumina Columns

Moore and Ward (21) and Venugopalan and Kutschke (22) obtained a separation of H_2, HD and D_2 on strongly activated alumina without an ortho-para separation. Moore and Ward activated the alumina for eight hours at 480°. Venugopalan and Kutschke used an activation temperature of 450° for one week. Both groups obtained chromatograms with noticeable peak tailing.

A column packing which required activation at approximately the same temperature necessary for catalyst activation would facilitate preparation of a heterogeneous column containing both a chromatographic separator and a reaction catalyst. If the peak tailing could be eliminated or greatly reduced, highly activated alumina mixed with a catalyst would represent a simply prepared chromatographic reactor.

A 10 foot column packed with 80-100 mesh alumina was activated

at 350° for one week under a low helium flow. This lower activation temperature was used with the anticipation that a reduction in the amount of peak tailing would be obtained, while retaining the ortho-para equilibration. Although the ortho-para isomers of H_2 and D_2 did not separate, the chromatogram peaks exhibited extreme tailing. Deuterium emerged from the column with an apparent retention time of 34 minutes compared to 14 minutes for hydrogen, giving a relative retention ratio of 2.44 for deuterium.

In an attempt to improve the peak symmetry of separations obtained with the highly activated alumina column, partial deactivation was attempted. Carbon dioxide was passed through the column until it was detected at the exit using a barium hydroxide solution. The column was cooled to 77° K. and the helium flow started. Peak shape was greatly improved; however, the ortho-para isomers of hydrogen completely separated. Para-hydrogen, ortho-hydrogen and ortho-para deuterium had retention times of 5.20, 6.00, and 8.67 minutes, respectively. Ortho and para deuterium did not separate.

It is possible that less carbon dioxide deactivation or a lower initial activation temperature would retain the ortho-para equilibrium and improve the peak symmetry. However, the peak shapes obtained with the carbon dioxide treatment did not appear to warrant further investigation. Strongly activated alumina columns were not suitable for use in this work.

Molecular Sieve 13X - Ferric Oxide Columns

Several columns were filled with 80-100 mesh Molecular Sieve 13X

packing that had been coated with ferric oxide to promote ortho-para isomerism. The packing was prepared by adding approximately 20 ml. of 1.8 molar ferric chloride to 40 ml. of 80-100 mesh Molecular Sieve 13X until the packing was completely dampened. Fifty ml. of water was added and the slurry titrated to a pH of 7.0 with 3.0 molar ammonium hydroxide (required approximately 36-40 ml.). The slurry was washed and decanted several times until the packing was free of the excess ferric hydroxide precipitate, leaving a small amount adsorbed on the packing. The packing was dried 24 hours at 120°, sieved, and the 80-100 mesh range poured directly into the column.

A three foot column of the above packing was activated at 165° for two days under a low helium flow. At 77° K. the Molecular Sieve 13X - ferric oxide column produced chromatograms with extreme tailing, but no ortho-para separation. Hydrogen and deuterium had apparent retention times of 4.8 and 12.6 minutes, respectively.

In an attempt to reduce the peak asymmetry, a six foot column was activated at 25° for 16 hours. Chromatograms with improved peak symmetry were obtained, although some tailing was still evident.

Since partial deactivation of the previous alumina column improved the peak shape, the six foot Molecular Sieve 13X - ferric oxide column was saturated with carbon dioxide at room temperature. After cooling to 77° K., the helium carrier gas flow was started. Hydrogen and deuterium peak shapes were quite acceptable, with little noticeable tailing. However, these peaks were not completely separated as they had been before the carbon dioxide treatment.

Numerous references in the literature have been made to the fact that Molecular Sieves irreversibly adsorb carbon dioxide. To test this statement, the six foot column was heated to 120° for three hours with a low helium flow. When used to separate hydrogen and deuterium at 77° K., extremely skewed peaks were obtained with a large separation. This result indicated that carbon dioxide was readily removed from the column on heating and not irreversibly adsorbed.*

A subsequent carbon dioxide treatment of this column, gave results slightly superior to those obtained on the Molecular Sieve 13X - ferric oxide column previously treated with carbon dioxide. Hydrogen and deuterium had apparent retention times of 1.57 and 2.52 minutes, respectively.

In order to provide sufficient separation of a mixture of H_2, HD and D_2, a 20 foot column filled with 70-80 mesh Molecular Sieve 13X ferric oxide was prepared. After activation at 120° for 12 hours, the column was partially deactivated with carbon dioxide as previously outlined.

A good separation of hydrogen and deuterium was obtained with apparent retention times of 6.16 and 9.43 minutes, respectively. However, each peak exhibited such a high effective diffusional spreading that a good separation of H_2, HD and D_2 would be impossible.

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*This apparent conflict between the experimental results of this investigation and previous chromatographic literature is readily resolved. Carbon dioxide has an extremely long retention time in Molecular Sieve columns, but is not irreversibly adsorbed.

Activated Alumina - Ferric Oxide Columns

A 12 foot chromatographic column was packed with 80-100 mesh alumina coated with ferric oxide. This packing was prepared in the same manner outlined for the Molecular Sieve 13X - ferric oxide column packing. After activation at 120° for one day with a low helium flow, the resulting chromatogram showed bad peak tailing, but no ortho-para separation.

A similarly prepared nine foot column was activated at 25° for 16 hours. Upon cooling to 77° K., the exit chromatogram exhibited much more symmetrical peak shapes, but with less separation. Subsequent carbon dioxide treatment followed by a 10 minute column purge with helium before cooling, offered no improvement. Carbon dioxide partial deactivation without a purge gave a slight improvement in the deuterium peak symmetry.

The 12 foot column which had been previously activated at 120° was treated with carbon dioxide and immediately cooled in liquid nitrogen. A chromatogram of hydrogen and deuterium was obtained equal to the results for the column activated at 25°.

In order to obtain sufficient separation between hydrogen and hydrogen deuteride, a 20 foot column of 70-80 mesh alumina coated with ferric oxide was activated at 120° for 12 hours. After activation, the column was treated with carbon dioxide and immediately immersed in liquid nitrogen.

Tests were performed to determine the carrier gas flow rate giving the best separation. It was found that an exit flow rate of

helium measured at room conditions of 110 ml./min. was optimum. The use of 70-80 mesh packing in place of the normal 80-100 mesh did not hurt the separation and required only half the pressure drop.

At the optimum flow rate, a 2.0 ml. sample of H_2, HD and D_2 equilibrated at 1000° K. gave a good H_2-HD separation and an excellent HD-D_2 separation. Peak symmetry was equal to any previous columns used in this work. Retention times of 5.80, 6.32, and 7.93 minutes were recorded for H_2, HD and D_2, respectively.

Chemical Amplifier

With helium as a carrier gas, large samples of the isotopes of hydrogen are required because of the small difference in thermal conductivity between helium and hydrogen. Also helium-hydrogen mixtures have a rapidly varying and anomalous thermal conductivity relation with concentration. In order to eliminate these problems, a copper oxide furnace was constructed which would oxidize the hydrogen isotopes. A thermal conductivity detector using a helium carrier gas is much more sensitive to the oxides of hydrogen isotopes than to the isotopes themselves. In effect, the copper oxide furnace acts as a chemical amplifier.

Other workers (21,22,23,26,27) have used a chemical amplifier with furnace temperatures from 416° to over 750°. A detector temperature above 100° is required to prevent condensation. Other reported details of construction are very sketchy. Copper oxide wire, 35-48 mesh copper oxide, fine copper oxide powder, and copper oxide powder mixed with firebrick have been used. All these forms of copper oxide

have drawbacks. Powders have sufficient surface area, but large pressure drops. The large mesh copper oxide has no appreciable pressure drop, but very little surface area. All methods appear to require excessive reactor volume to permit sufficient contact time.

A high surface form of copper oxide is needed which can be prepared in any desired mesh range. This requirement was met in this investigation by completely wetting a 80-100 mesh sample of Chromosorb-P (a diatomaceous earth product manufactured by the Johns-Manville Co.) and a 80-100 mesh sample of alumina with a saturated solution of cupric nitrate. After drying overnight at 105°, each sample was reduced to the oxide form at 700° in a furnace for two hours. Both samples were sieved to 80-100 mesh and packed in separate four inch long, one-fourth inch outside diameter stainless steel combustion tubes constructed such that they could be inserted in the chromatographic system before the detector.

It was expected that alumina with its much larger surface area (210 $m.^2/gm.$) would be more efficient than Chromosorb-P (4 $m.^2/gm.$). However, alumina exhibited adsorption even at the high temperatures used and produced extremely diffused chromatogram peaks.

Chromosorb-P did not display any peak spreading properties during the tests to determine the optimum operating temperature for the chemical amplifier. No signal amplification was noted below 200°. Between 200° and 400° the amplification increased steadily, reaching a plateau above 400°. No change in amplification was found as high as 500°. It was therefore decided to use the chemical amplifier at 450°

where it possessed a signal amplification of about 34. This amplification is equivalent to using a sample 34 times as large for the same response without a chemical amplifier.

Chromatograms obtained using the chemical amplifier following the 20 foot activated alumina - ferric oxide column were quite satisfactory with total separation of HD and D_2 and sufficient separation of H_2 and HD. It was estimated that a 40 foot column would completely separate all the components.

If a H_2-D_2 exchange reaction catalyst capable of operation at the temperature required for chromatographic separation were available, a heterogeneous chromatographic packing could be made from a mixture of the catalyst and the previously developed, activated alumina - ferric oxide packing.

Hydrogen Exchange Reaction Catalyst Tests

A review of the literature indicated that reaction catalysts of chromium, nickel, and iron should be effective in promoting the exchange reaction between hydrogen and deuterium. One sample each of a chromium catalyst and a nickel catalyst and three iron catalysts were obtained for an evaluation of their effectiveness.

Equipment

A five inch section of stainless steel tubing with a one-fourth inch outside diameter was wrapped with nichrome heater wire and insulated to provide temperatures in excess of 500°. The tubing had an internal volume of approximately 1.5 cc. Sieved catalysts were packed in this small tubular reactor and activated at the prescribed conditions under

a reducing carrier of Matheson prepurified hydrogen (minimum purity 99.95 percent). During activation a one foot Molecular Sieve 13X column was attached to the reactor entrance and another to the exit to prevent impurities that might poison the catalyst from entering the reactor.

After activation and cooling to room temperature, the reactor was placed in the chromatographic system immediately before the 20 foot activated alumina - ferric oxide column. This placement allowed direct analysis of the reaction mixture leaving the tubular reactor. Also it was unnecessary to construct a heterogeneous chromatographic reactor (capable of simultaneous reaction and separation) for each catalyst test.

Chromium Oxide Catalyst

A chromium oxide catalyst, Cr-1404P, was obtained from The Harshaw Chemical Company. The catalyst contained 19 percent Cr_2O_3, supported on high activity alumina with a surface area of 80-100 $m.^2/gm.$ After sieving the catalyst, a 100-120 mesh range was activated for two hours at 300° in the tubular reactor.

At room temperature with a helium exit flow rate of 105 ml./min., the catalyst converted an equal molar mixture of hydrogen and deuterium to essentially an equilibrium mixture. At this flow rate, the reactor residence time was approximately 2.5 seconds.

Because of the extremely rapid reaction at room temperature, catalyst tests were undertaken at 77° K. However, no reaction was found to occur at 77° K. even though the residence time had been extended to approximately 10 seconds. In addition, the catalyst greatly

retarded the hydrogen - deuterium sample giving increased retention times for both components. This increased retention resulted in an extremely diffused chromatogram, unsuitable for use in an investigation of the chromatographic reactor concept.

The diffused chromatogram was believed to be due to the activated alumina catalyst support. Previous experiments with chromatographic columns indicated a possible improvement with a carbon dioxide treatment of the support material prior to the catalyst test. While carbon dioxide treatment reduced the peak spreading, no reaction was found at 77° K. In addition, the carbon dioxide poisoned the reaction catalyst such that no reaction occurred at room temperature. The chromium oxide catalyst would not be useful in this work.

Nickel Catalyst

A nickel catalyst used commercially to promote the hydrogen-deuterium exchange reaction was obtained from the Girdler Catalysts department of Chemetron Chemicals. Girdler nickel catalyst T-316 was supplied in three-sixteenths inch tablets composed of 50 percent nickel on a kieselguhr support. The recommended activation was two hours at 150°-315° in a stream of hydrogen. The catalyst was ground and sieved to a 80-100 mesh range and packed into the tubular reactor.

After two hours activation at 300°, the catalyst was tested at room temperature. An unexpected result was found. On injection of the first equal molar mixture of hydrogen and deuterium, only a hydrogen peak appeared on the chromatogram. With subsequent injections hydrogen and hydrogen deuteride appeared. Finally all three isotopic variations

emerged from the column in equilibrium concentrations. The nickel catalyst preferentially adsorbed deuterium and desorbed hydrogen until an equilibrium mixture had been adsorbed on the catalyst surface.

The nickel catalyst was cooled to 77° K. and tested. Extreme catalyst adsorption, long retention times, and no apparent reaction made this catalyst useless for the hydrogen isotope exchange reaction in a chromatographic reactor at 77° K. The dependence of the reaction products on the previous injected reactants found at room temperature also eliminated the nickel catalyst.

Iron Catalysts

Three iron catalysts were tested for the hydrogen-deuterium exchange reaction: Harshaw Chemical Company Fe-0303P catalyst, Girdler G3A singly-promoted catalyst, and a singly-promoted iron catalyst received from Dr. P. H. Emmett, catalyst 385.

Catalyst Fe-0303P. Harshaw Catalyst Fe-0303P contained 20 percent Fe_2O_3 mounted on high activity alumina with a surface area of 105 $m.^2/gm.$ After sieving, the 100-120 mesh range was activated two hours at 300° under a hydrogen carrier.

At room temperature an equal molar mixture of hydrogen and deuterium reacted to give about 10 mole percent hydrogen deuteride. An equilibrium mixture at this temperature contains 47 percent hydrogen deuteride. The approximate time required for half conversion was calculated to be 12 seconds.

A test of the catalyst at 77° K. revealed no apparent reaction. Again, the activated alumina catalyst support retarded and spread the

hydrogen-deuterium sample passing through the reaction catalyst.

Catalyst G3A. Girdler catalyst G3A is a iron catalyst singly promoted with chromium. An activation of two hours at 260-315° in a stream of hydrogen was recommended by the manufacturer. The catalyst was received in three-eighth inch tablets which were subsequently crushed and sieved to 80-100 mesh.

At room temperature the catalyst converted an equal molar mixture of hydrogen and deuterium to essentially equilibrium. The chromatogram showed no additional spreading caused by the catalyst.

No apparent reaction was found at 77° K. However, the retention times on the catalyst were of the same magnitude as for the alumina column alone. Also the separation ratio of hydrogen and deuterium was much greater than previously experienced on chromatographic columns. Although producing more diffused chromatograms, the iron catalyst alone actually could have separated the reaction mixture because it retarded deuterium more than it retarded hydrogen.

Treatment of the catalyst with carbon dioxide was performed to determine whether or not this would poison the catalyst at room temperature. The reaction was greatly retarded, although some hydrogen deuteride was still produced. After reactivation at 300° for two hours, the original fast reaction rate was restored.

A four foot column with an internal volume of 2.7 cc. was packed with 80-100 mesh G3A catalyst. It was thought that the longer contact time and the apparent selective adsorption of deuterium on the catalyst would permit a reaction and separation of the hydrogen isotopes. After

activation at 300° for two hours, the four foot catalyst column offered only slight separation at 77° K. and no apparent reaction.

In an effort to insure that the catalyst had been properly activated, the catalyst column was warmed to room temperature and the chromatographic alumina-ferric oxide column added to the system. An equal molar mixture of hydrogen and deuterium reacted at room temperature and again gave essentially equilibrated reaction products. Apparently the catalyst was properly activated.

P. H. Emmett Catalyst 385. After the previous failures to obtain a H_2-D_2 exchange reaction at 77° K. using chromium, nickel, and iron catalysts, a sample of the singly-promoted iron catalyst 423 used by Kummer and Emmett (30) was requested from Dr. P. H. Emmett. Although the supply of catalyst 423, which gave the extremely rapid H_2-D_2 exchange reaction at 77° K., was exhausted, a 10 gram sample of catalyst 385 was supplied. The catalyst contained 0.83 percent alumina, 1.63 percent silica, and 0.45 percent beryllium oxide, in addition to iron oxide. This catalyst should act as a singly-promoted catalyst. Activation at 500° for two or three days at a hydrogen space velocity of 5000 was recommended by Dr. P. H. Emmett to produce a very active catalyst usable at 77° K.

Catalyst 385 was activated at 500° for three hours with a hydrogen space velocity of about 5000. At room temperature the exchange reaction was practically instantaneous, giving hydrogen deuteride in an equilibrium mixture from an equal molar mixture of hydrogen and deuterium. The chromatogram exhibited no additional tailing or peak spreading

caused by the catalyst.

Cooling the catalyst to 77° K. completely stopped the reaction. One distinct feature of catalyst 385 at 77° K. was the complete absence of any peak spreading caused by the catalyst.

A longer activation was undertaken to comply with the recommended activation time. Catalyst 385 was activated for 48 hours at 500° with a hydrogen space velocity of 5000. Molecular Sieve 13X columns were placed before and after the catalyst reactor to prevent water and oxygen contamination. A carrier gas preheater was constructed to insure that the entering hydrogen was above 500°.

Following this activation, the tubular reactor was placed in the chromatographic system prior to the 20 foot activated alumina-ferric oxide column and cooled to 77° K. The helium carrier gas was further purified by passing through a six foot Molecular Sieve 13X column cooled to 77° K. With all these precautions and the long activation, no reaction occurred between hydrogen and deuterium at 77° K.

Tests of chromium, nickel, and iron catalysts have not produced any catalyst capable of operating at a temperature of 77° K. Several of the catalysts gave an almost instantaneous reaction between hydrogen and deuterium at room temperature.

Chromatographic Reactor Data

Two chromatographic columns, 10 and 20 feet long, were constructed to provide nonreactive chromatographic data for a comparison with the numerical solutions of the equations describing the mathematical model. The columns were filled with the 70-80 mesh alumina - ferric

oxide packing previously described.

To provide the maximum separation of H_2, HD and D_2, a final comparison of the various activation temperatures and carbon dioxide partial deactivation treatments was undertaken. The 10 foot column was activated at 25° for 14 hours with a helium flow rate of 25 ml./min. At 77° K. and an exit flow of 110 ml./min., this column gave a retention ratio of 1.28 for deuterium relative to hydrogen. The column was subsequently treated with carbon dioxide and immersed in liquid nitrogen before starting the helium carrier flow. This treatment gave a relative retention ratio for deuterium of 1.21. The carbon dioxide treatment had little effect. In both cases the separation of H_2 and D_2 was only marginal.

Column activation at 120° for 20 hours gave a chromatogram with diffused peaks and extreme tailing. Retention times for hydrogen and deuterium of 10.81 and 18.38 respectively, gave a relative retention ratio of 1.70 for deuterium. Carbon dioxide treatment at room temperature followed by a 10 minute helium purge before cooling in liquid nitrogen did not significantly alter the chromatogram.

Another carbon dioxide treatment of the 10 foot column was performed followed by immediate immersion in liquid nitrogen before starting the carrier flow. This treatment greatly improved the chromatogram peak shape and only reduced the retention ratio of deuterium to 1.39. Retention times for H_2, HD and D_2 were 3.88, 4.24 and 5.41 minutes, respectively.

Optimum column treatment, as determined from these experiments,

consisted of 20 hours activation at 120° with a low helium flow rate, cooling to room temperature under helium, followed by passing an excess of carbon dioxide through the column at room temperature. The column was immediately immersed in liquid nitrogen and partially cooled before starting the helium carrier gas flow. An optimum exit flow rate of 110 ml./min. was maintained.

Using these optimum conditions and the chemical amplifier, chromatograms of H_2-HD-D_2 mixtures were obtained for the 10 and 20 foot columns. Samples of equal molar mixtures of H_2 and D_2, equilibrated at 1000° K. over a hot wire filament, were injected into the carrier gas stream using a Hamilton gas-tight syringe. With the aid of equations developed in Appendix C, reduced constants were calculated for 500 microliter samples of the H_2-HD-D_2 mixture for the 10 and 20 foot columns.

For the 20 foot activated alumina - ferric oxide column, the reduced constants are:

$$D^{o}_{H2} = D^{o}_{b} = 0.000346$$

$$D^{o}_{HD} = D^{o}_{a} = 0.000382$$

$$D^{o}_{D2} = D^{o}_{c} = 0.000284$$

$$R^{o}_{H2} = R^{o}_{b} = 1.104$$

$$R^{o}_{HD} = R^{o}_{a} = 1.000$$

$$R^{o}_{D2} = R^{o}_{c} = 0.8027$$

For the 10 foot activated alumina - ferric oxide column, the reduced constants are:

$$D^{o}_{H2} = D^{o}_{b} = 0.000594$$

$$D^{\circ}_{HD} = D^{\circ}_{a} = 0.000773$$

$$D^{\circ}_{D2} = D^{\circ}_{c} = 0.000517$$

$$R^{\circ}_{H2} = R^{\circ}_{b} = 1.097$$

$$R^{\circ}_{HD} = R^{\circ}_{a} = 1.000$$

$$R^{\circ}_{D2} = R^{\circ}_{c} = 0.7876$$

Using the reduced constants, numerical solutions were obtained for comparison with the experimental chromatograms. Experimental and numerical chromatograms are shown in Figures 5 and 6 for the 20 and 10 foot columns, respectively.

The main difference between the experimental and the numerical or calculated chromatograms is due to the fact that the experimental chromatogram does not have symmetrical peaks. The experimental concentration curves rise abruptly, but exhibit tailing with decreasing concentration. This asymmetry has long plagued gas-solid chromatography and is usually believed to be due to the nonlinear adsorption isotherms of the solid adsorbents.

Several interesting papers have been published that cited other possible causes of asymmetric peaks. Scott (36) considered the change in temperature of an absorbent undergoing adsorption and desorption. It was shown that chromatogram peaks of the shape experienced in the present investigation could be caused entirely by heats of adsorption and desorption.

Giddings (37) concluded that peak tailing could originate as a kinetic effect of adsorption and desorption even with a linear adsorption isotherm. It was noted for linear isotherms, that tailing

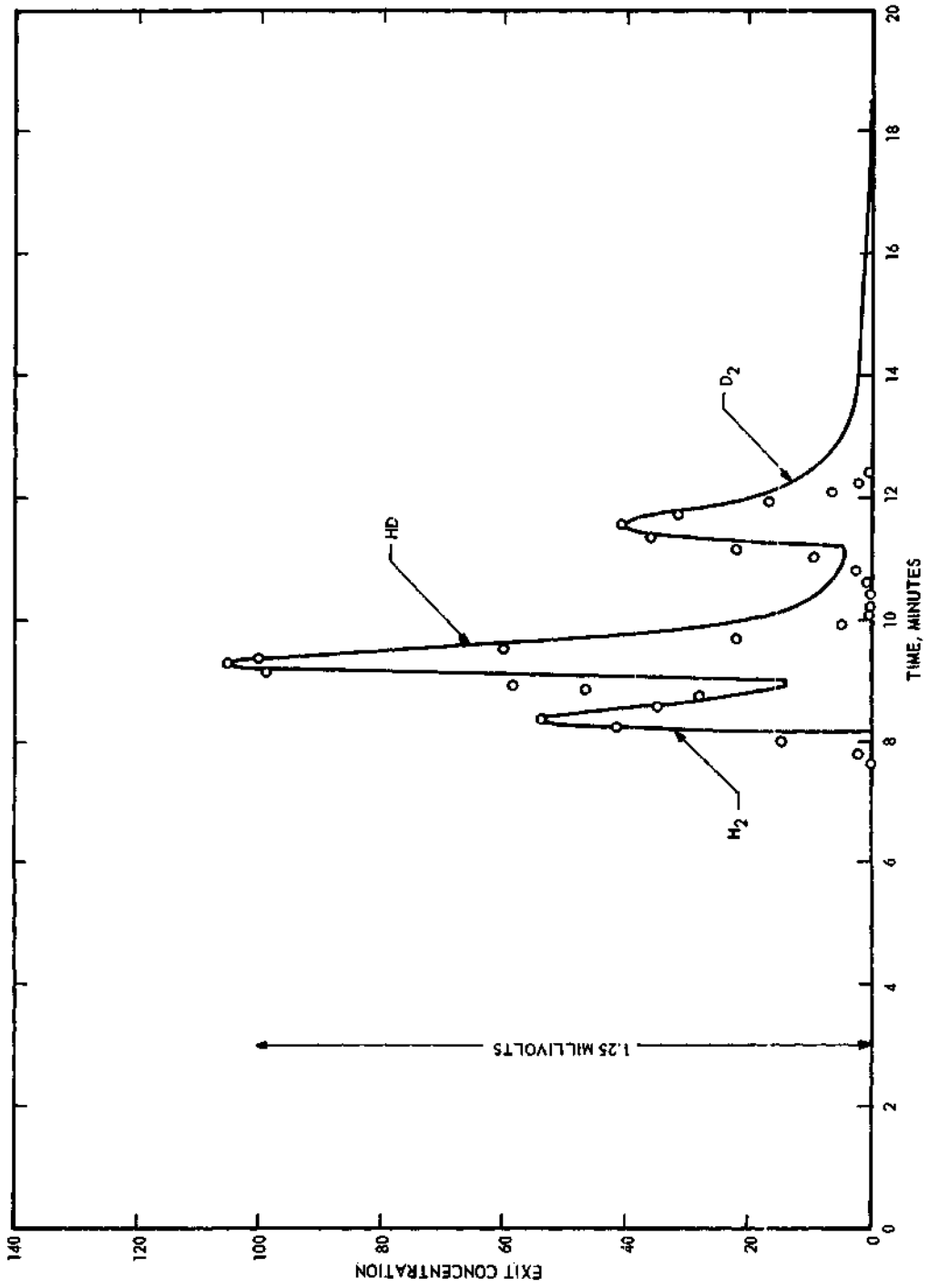

Figure 5. Comparison of Experimental and Numerical Chromatograms for H_2-HD-D_2 Separation with No Reaction in a 20 foot Alumina - Ferric Oxide Column.

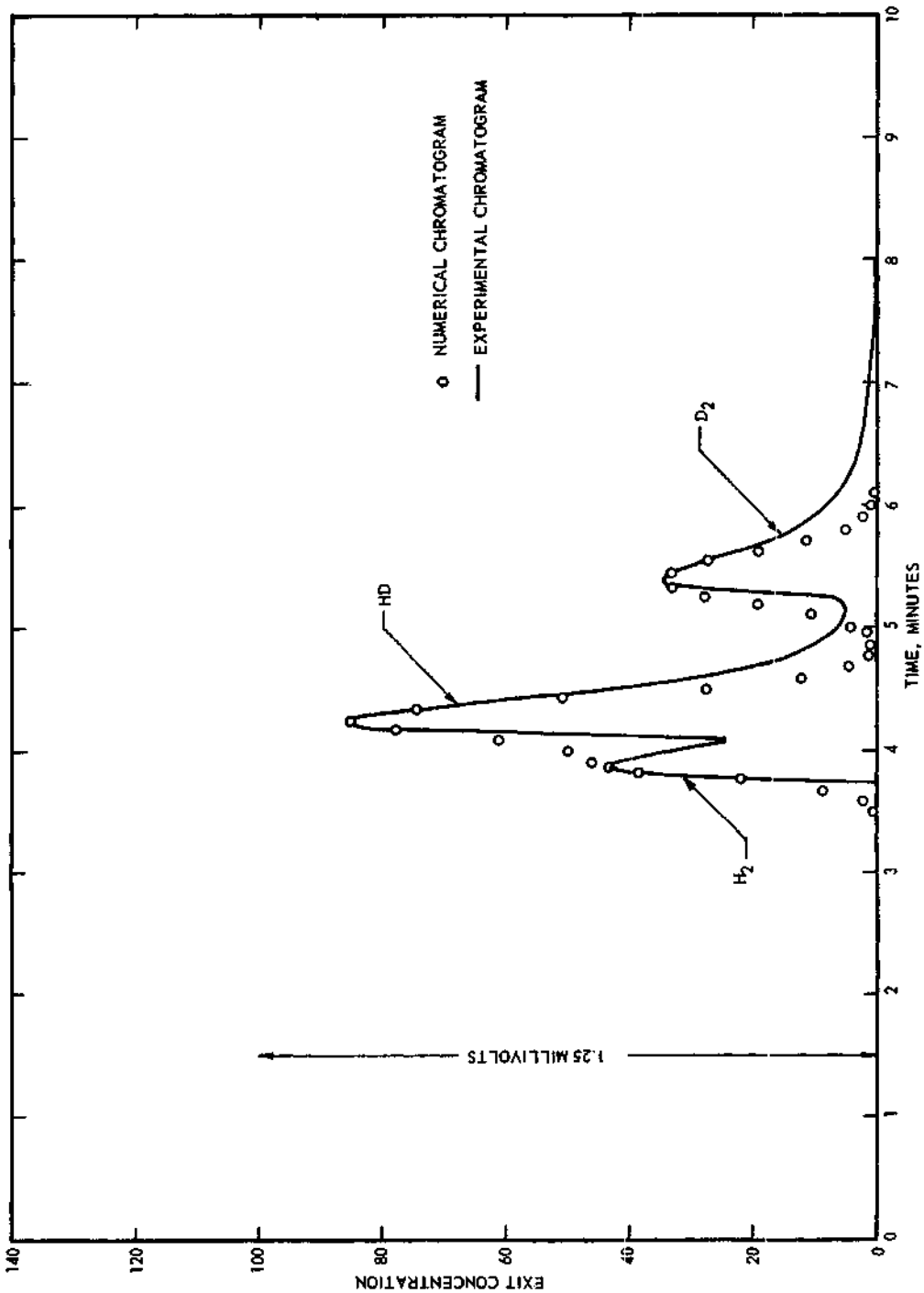

Figure 6. Comparison of Experimental and Numerical Chromatograms for H_2-HD-D_2 Separation with No Reaction in a 10 foot Alumina - Ferric Oxide Column.

will not significantly decrease with sample size; while for nonlinear isotherms, tailing will be reduced with smaller samples. Kinetic tailing will increase with increasing column velocity, whereas tailing caused by nonlinear isotherms will be little affected.

A more detailed numerical chromatogram was calculated with the reduced constants of the 10 foot activated alumina - ferric oxide column. For an equal molar mixture equilibrated at 77° K., the graph is shown in Figure 7 with the time axis given in its reduced form. The individual component concentrations are included as well as the composite chromatogram.

The reduced reaction rate constants for the hydrogen-deuterium exchange reaction were calculated using the data of Kummer and Emmett (30) and Appendix C. The results of these calculations for the 10 foot chromatographic column gave the forward and reverse reduced rate constants as 11 and 21 $(\text{moles/l.})^{-1}$, respectively. Using these reduced reaction rate constants and the nonreactive experimental data, a numerical chromatogram was calculated to determine the amount of HD which would have been converted if a reaction had occurred. This chromatogram is presented in Figure 8 for the same equilibrium sample used with the previous graph.

The theoretical 10 foot column has reduced the computer calculated HD mole fraction from an initial equilibrium mole fraction of 0.408 to 0.123. Despite the slight H_2-HD separation in this column, it is readily seen that a considerable improvement has been realized using a chromatographic reactor.

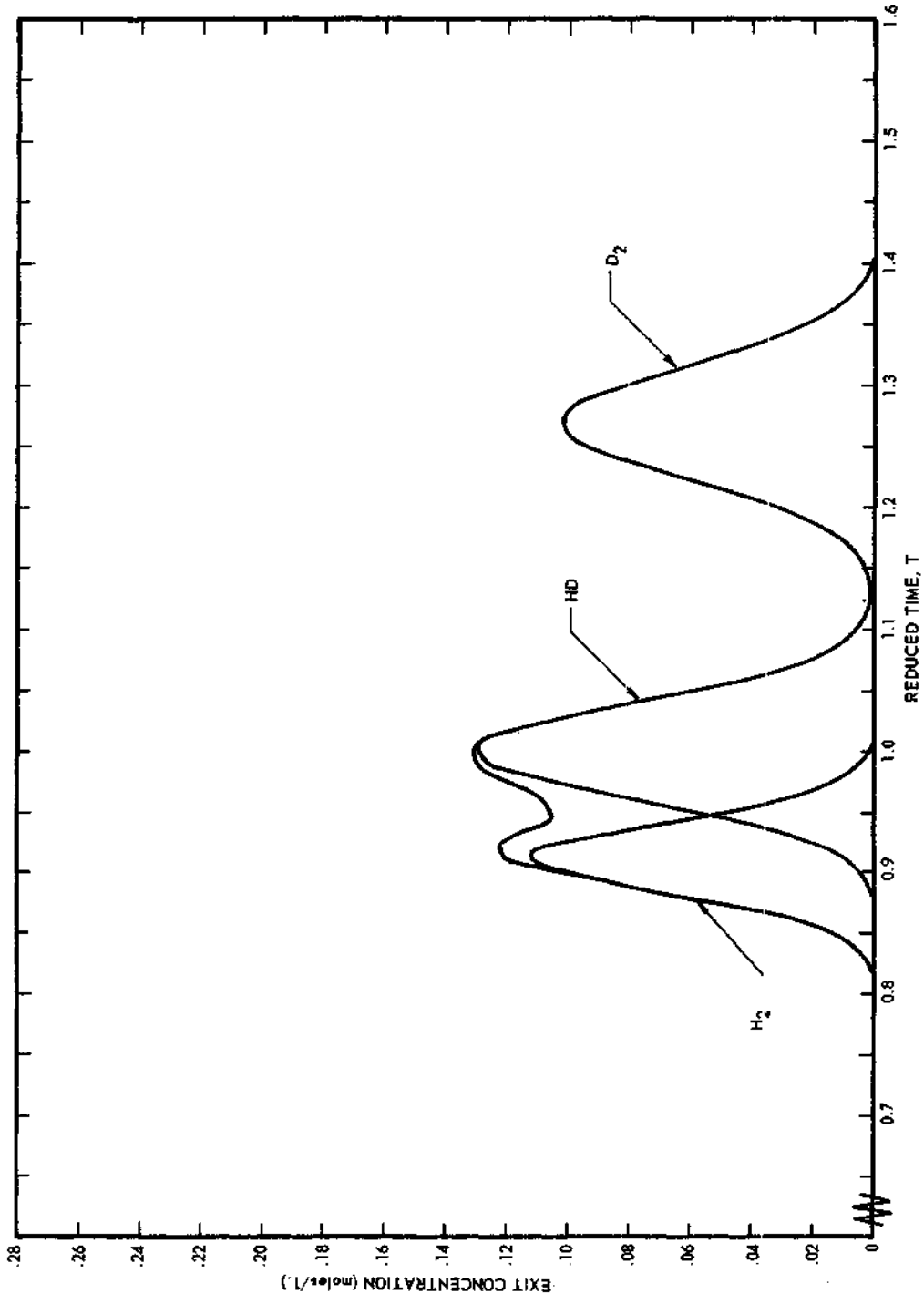

Figure 7. Numerical Chromatogram of H_2-HD-D_2 Separation with No Reaction in a 10 foot Alumina - Ferric Oxide Column.
Total Feed Concentration: 10.0 moles/l.

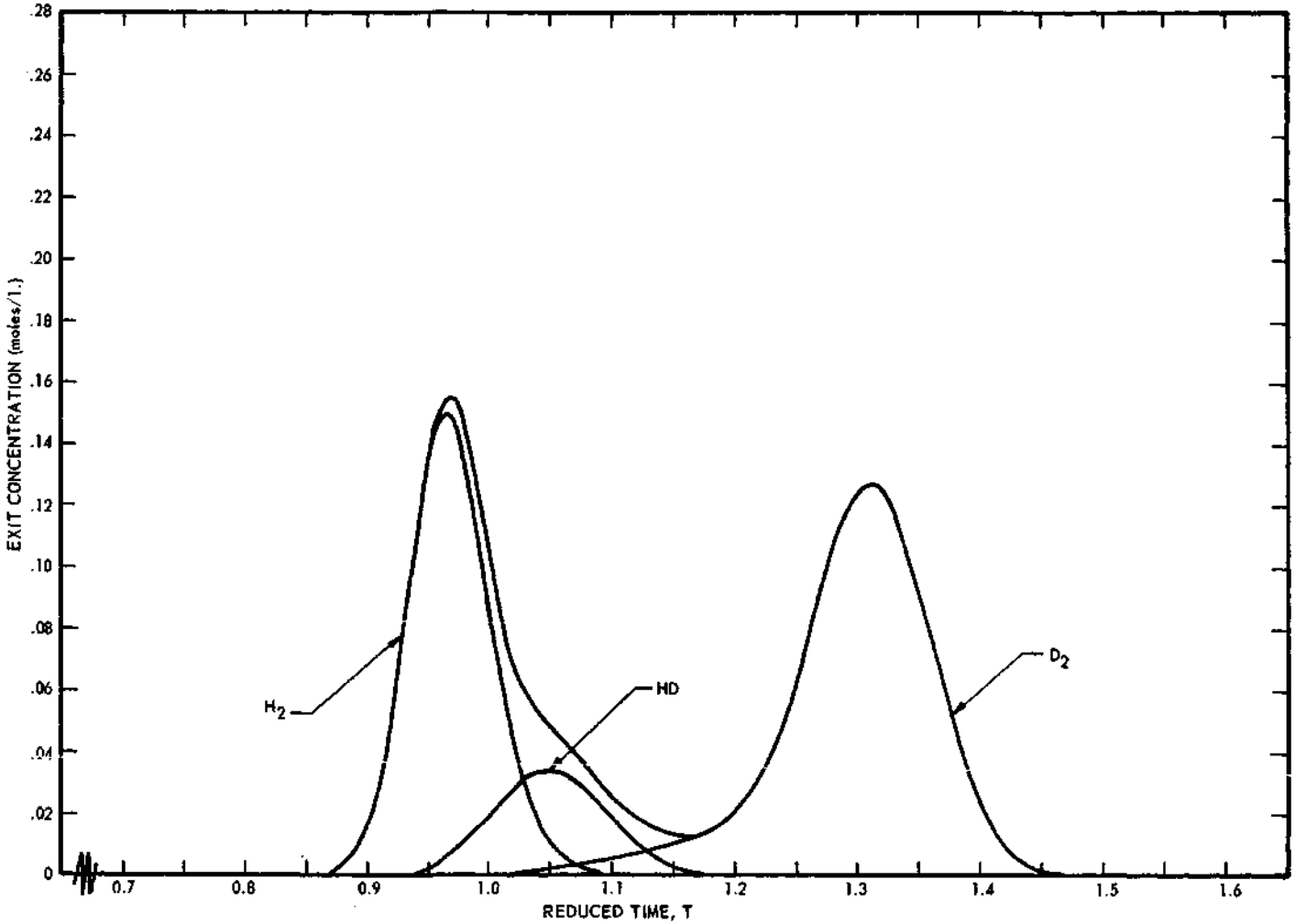

Figure 8. Numerical Chromatogram of the Reaction $2HD = H_2 + D_2$ in a 10 foot Alumina - Ferric Oxide Column.
Reduced Forward Reaction Rate, $k_1^0 = 11$ (moles/l.)$^{-1}$.
Reduced Reverse Reaction Rate, $k_2^0 = 21$ (moles/l.)$^{-1}$.
Total Feed Concentration: 10.0 moles/l.

The calculations for the reduced reaction rate constants for the 20 foot alumina - ferric oxide column gave a value of 24 $(moles/l.)^{-1}$ for the reduced forward rate constant and 46 $(moles/l.)^{-1}$ for the reduced reverse rate constant. The reduced reaction rate constants for the 20 foot column are not exactly twice the values for the 10 foot column because the reactant retention time on the 20 foot column was greater than twice the retention time on the 10 foot column. The reduced reaction rate constant was defined in Appendix C as the product of the actual reaction rate constant and the reactant retention time. The nonreactive chromatogram for the 20 foot column is given in Figure 9 and the reactive chromatogram in Figure 10. The HD exit mole fraction for the 20 foot column with reaction is 0.0536. This amount is less than half the amount for the 10 foot column.

An additional advantage of the longer column is the greater separation between H_2 and HD. By proper switching of the exit affluent, essentially pure H_2 and D_2 can be obtained and the remaining portion recycled to the column feed.

In the experimental part of this investigation an activated alumina - ferric oxide column was developed capable of separating a H_2-HD-D_2 mixture. Experimental nonreactive data from this column were used for a comparison with the numerical solutions to the equations describing the chromatographic reactor model. The main difference between the experimental and numerical chromatograms is due to the fact that the experimental chromatogram does not have symmetrical peaks. The nonreactive data of this investigation and the H_2-D_2 exchange

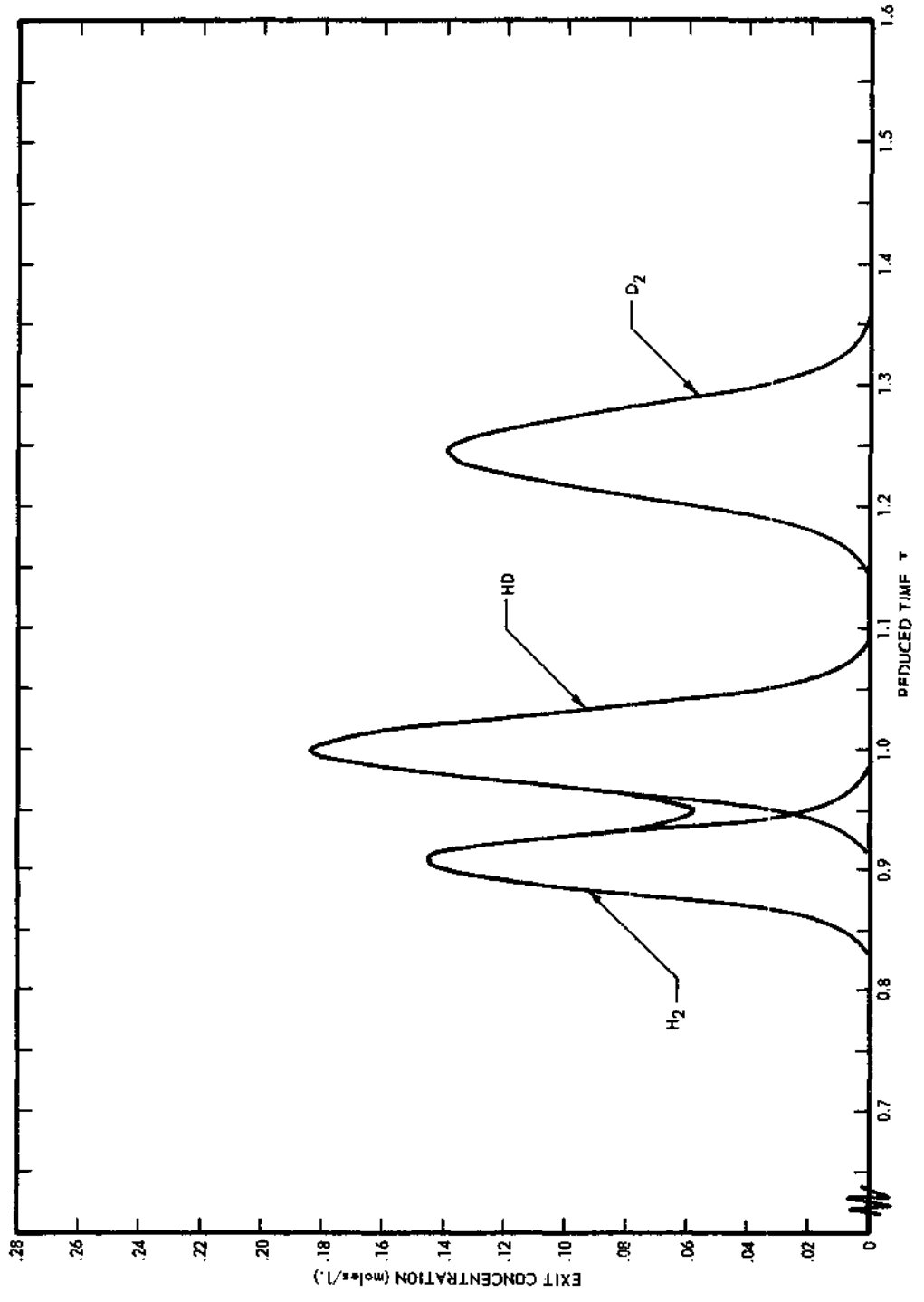

Figure 9. Numerical Chromatogram of H_2-HD-D_2 Separation with No Reaction in a 20 foot Alumina - Ferric Oxide Column.
Total Feed Concentration: 10.0 moles/l.

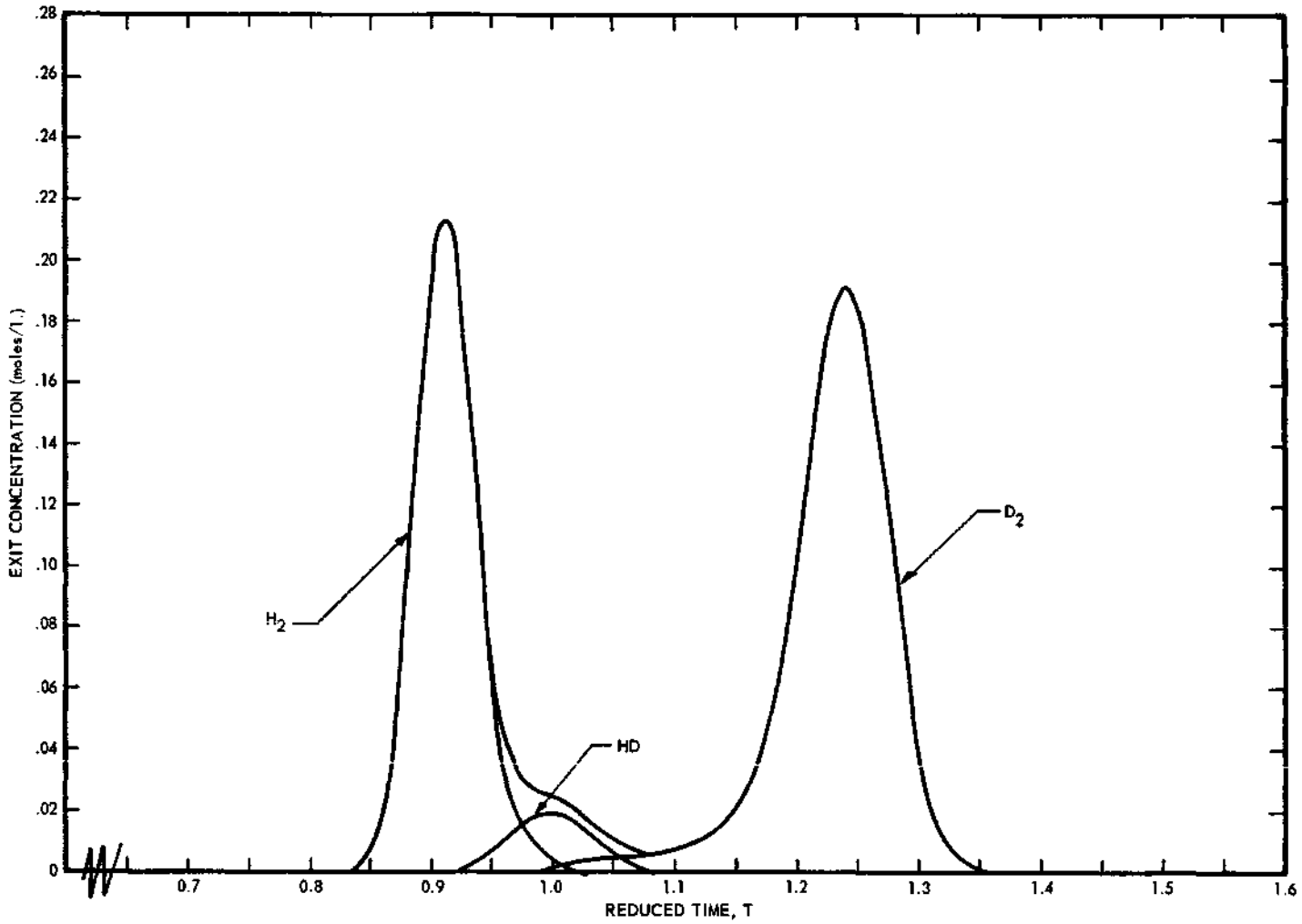

Figure 10. Numerical Chromatogram of the Reaction $2HD = H_2 + D_2$ in a 20 foot Alumina - Ferric Oxide Column.
Reduced Forward Reaction Rate, $k_1^o = 24$ (moles/1.)$^{-1}$.
Reduced Reverse Reaction Rate, $k_2^o = 46$ (moles/1.)$^{-1}$.
Total Feed Concentration: 10.0 moles/1.

reaction data of Kummer and Emmett (30) were used to calculate numerical chromatograms of the $2HD \rightleftarrows H_2 + D_2$ reaction occurring in a chromatographic reactor.

CHAPTER IV

NUMERICAL SOLUTIONS

The primary purpose of this investigation was to obtain solutions to the nonlinear equations describing the chromatographic reactor model for the reaction $2A \rightleftarrows B + C$. These equations were developed in Chapter II. A numerical method for solution of the equations is given in Appendix A along with a discussion of its stability, convergence and error. The computer program of the numerical solution scheme is included in Appendix B.

The numerical solutions for nonreactive chromatographic columns are compared to the available analytical solutions in Chapter II and to experimental data in Chapter III. Using the experimental data of Chapter III and the reaction rate constants calculated from the data of Kummer and Emmett (30), numerical chromatograms were calculated for the reaction and separation of a H_2-HD-D_2 mixture.

A complete solution to Equations (5), (6), and (7) involves eight parameters plus the required initial conditions. These parameters are D_a^o, D_b^o, D_c^o, k_1^o, k_2^o, R_a^o, R_b^o, and R_c^o. Certain assumptions were made concerning these parameters in order to cover a large range of values without using an excessive amount of computer time. The reduced effective diffusion coefficients of all three components were assumed equal ($D_a^o = D_b^o = D_c^o$). For the numerical solutions the ratio of reduced forward reaction rate constant, k_1^o, to the reduced reverse

reaction rate constant, k_2^o, was taken equal to the equilibrium constant,* K_e. The equilibrium constant was generally set equal to 0.500, although other values were used. (For the reaction $2HD \rightleftarrows H_2 + D_2$, the equilibrium constant at 77^o K. is approximately 0.526 (31).) The total initial concentration, $(A_o + B_o + C_o)$, was taken equal to 10 moles/l. Usually the individual initial concentrations were fixed to represent an equilibrium mixture of A, B and C with $B_o = C_o$. The effect of using a non-equilibrated feed was also studied.

The value of R_a^o was taken equal to 1.0. This choice is equivalent to stating that the maximum concentration of component A emerged at the reduced time of T = 1.0 for a nonreactive chromatogram. Relative values of R_i^o were taken such that $R_c^o > R_a^o > R_b^o$. (In a few cases other orders of column velocities were taken to test the effect on the product yield.) In reduced time units the nonreactive peak emergence time is given as $T_{Ri}^o = (1/R_i^o)$. A relation between the various peak emergence times was arbitrarily fixed as $T_R^o = (T_{Ra}^o - T_{Rc}^o) = (T_{Rb}^o - T_{Ra}^o)$, where T_R^o is called the reduced peak emergence time. This relation requires that the resulting nonreactive chromatogram have peaks that are equally separated in time. The retention time relationship can be rearranged to give $(R_b^o + R_c^o)/(2R_b^o R_c^o) = 1$.

In this investigation, the reduced effective diffusion coefficient, D_i^o, was varied from 0.00025 to 0.002. Extrapolations to zero

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*This choice assumes that the stoichiometric equation $2A \rightleftarrows B + C$ represents the reaction mechanism and that the reactant and products all obey the equation of state, PV = RT.

diffusion were made to extend the total range studied effectively to $0 \leq D_i^o \leq 0.002$. Seven values of the reduced reaction rate constants k_1^o and k_2^o, were taken from zero to 1000 (moles/l.)$^{-1}$. The effect of the equilibrium constant was studied for values of K_e of 0.001, 0.01, 0.1, 0.5, and 1.0. The three possible variations of the peak emergence order were also investigated.

Effect of Chromatographic Separation on Yield

The effect of the chromatogram peak separation was examined at four values of the reduced peak emergence time, T_R^o, chosen to cover the range expected in most chromatographic separations. These values were T_R^o = 0.10, 0.15, 0.25, and 0.50. The corresponding separation ratios (relation retention ratios) between the various component peaks can be calculated from the appropriate ratio involving only T_R^o. For the above T_R^o range, the separation ratio between the first and last emerging peak is between 1.22 and 3.00. (In this investigation the experimental H_2 - D_2 separation ratio ranged from 1.21 to 2.44.)

Many chromatographic separations are currently used with component separation ratios less than 1.22. However, the numerical solutions can be easily extrapolated to zero separation by remembering that the maximum reaction yield with no separation is equal to the batch reaction yield.

The effect of the peak separation, T_R^o, on the amount of reactant A remaining for a reduced effective diffusion coefficient, D_i^o, of 0.002 and an equilibrium constant, K_e, of 0.500 is shown in Figure 11 with the reduced forward reaction rate constant as a parameter. The

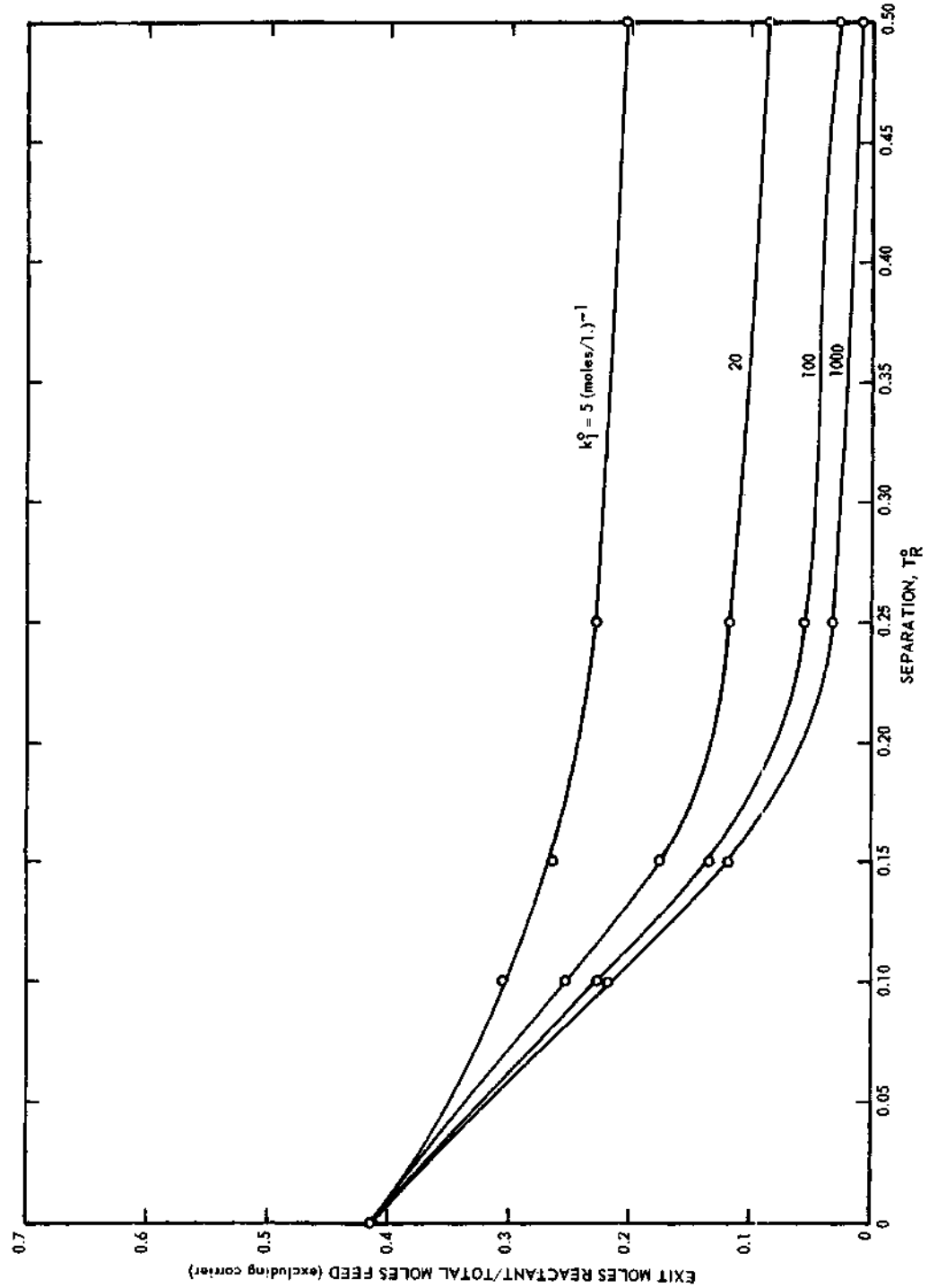

Figure 11. Effect of the Peak Separation on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Effective Diffusion Coefficient: 0.002.

mole fraction of reactant A was determined from the material balance calculated from the exit concentration chromatogram. Two facts should be noted from Figure 11. First, there is very little increase in conversion with separations, T_R^o, greater than 0.25. Second, reduced reaction rate constants greater than 100 $(\text{moles/l.})^{-1}$ do not offer a corresponding increase in yield.

A similar graph for a reduced effective diffusion coefficient, D_i^o, equal to 0.001 is offered in Figure 12. While exhibiting a somewhat parallel behavior to Figure 11, Figure 12 offers a much more rapid decrease in reactant for a corresponding increase in separation. However, the limited effectiveness of reduced reaction rate constants greater than 100 $(\text{moles/l.})^{-1}$ or reduced peak emergence times greater than 0.25 is still evident.

Effect of Diffusion on Yield

A good reduction in the amount of reactant remaining was noticed in Figure 12 when the reduced effective diffusion coefficient was halved. To determine the effect of diffusional spreading on the yield, numerical solutions were obtained at reduced effective diffusion coefficients of 0.00025, 0.0005, 0.001, and 0.002 for a range of reduced forward reaction rate constants, k_1^o, and reduced peak emergence times, T_R^o. The numerical solution scheme required an extremely fine grid mesh and a corresponding long calculating time for accurate calculations at low diffusion coefficients. In order that the curves might be extrapolated to zero diffusion, it was reasoned that with no diffusion and a rapid separation of products the minimum reactant remaining at any

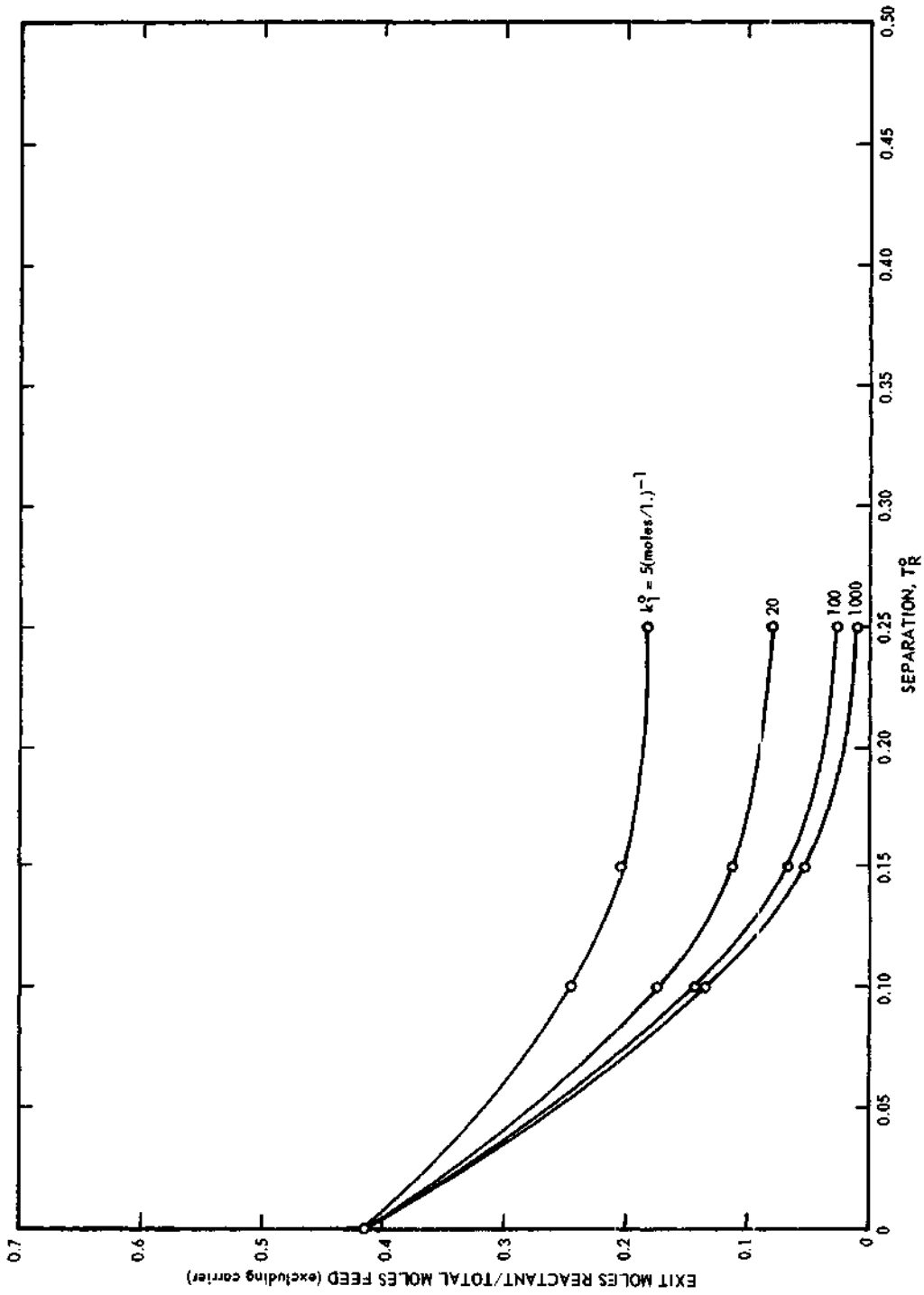

Figure 12. Effect of the Peak Separation on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Effective Diffusion Coefficient: 0.001.

time, T, could be calculated by integrating a limiting form of Equation (5). Equation (5) can be approximated, for nc diffusion and a rapid separation of products, as

$$\frac{\partial A}{\partial T} + R_A^o \frac{\partial A}{\partial X} = 2k_1^o A^2$$

Transforming the variable A from a function of X ard T to a function of Z and T gives

$$\frac{\partial A}{\partial T} = 2k_1^o A^2$$

where $Z = X - R_a^o T$. Integrating from zero time to time T = 1.00 (peak emergence time) with the independent variable Z held constant at Z = 0 gives $A(T = 1) = A_o/(1 + 2k_1^o A_o)$, where A_o is the initial concentration of reactant A.

For an equilibrium constant of 0.500 and a total molar concentration of 10 moles/l., an equilibrated feed, with $B_o = C_o$, would contain A_o = 4.142 moles/l. This value of the initial molar concentration of A_o was used with the above equation to calculate the limiting amount of reactant A remaining at zero diffusion.

The effect of the reduced diffusion coefficient on the amount of reactant remaining is shown in Figure 13, 14 and 15 for reduced peak emergence times, T_R^o, of 0.10, 0.15, and 0.25, respectively. It is evident that small diffusion coefficients are quite necessary at low component separations to insure a good reduction of the reactant, A. This effect is greatly pronounced for small reaction rate constants. As the diffusion coefficient approached zero, the exit mole fraction of

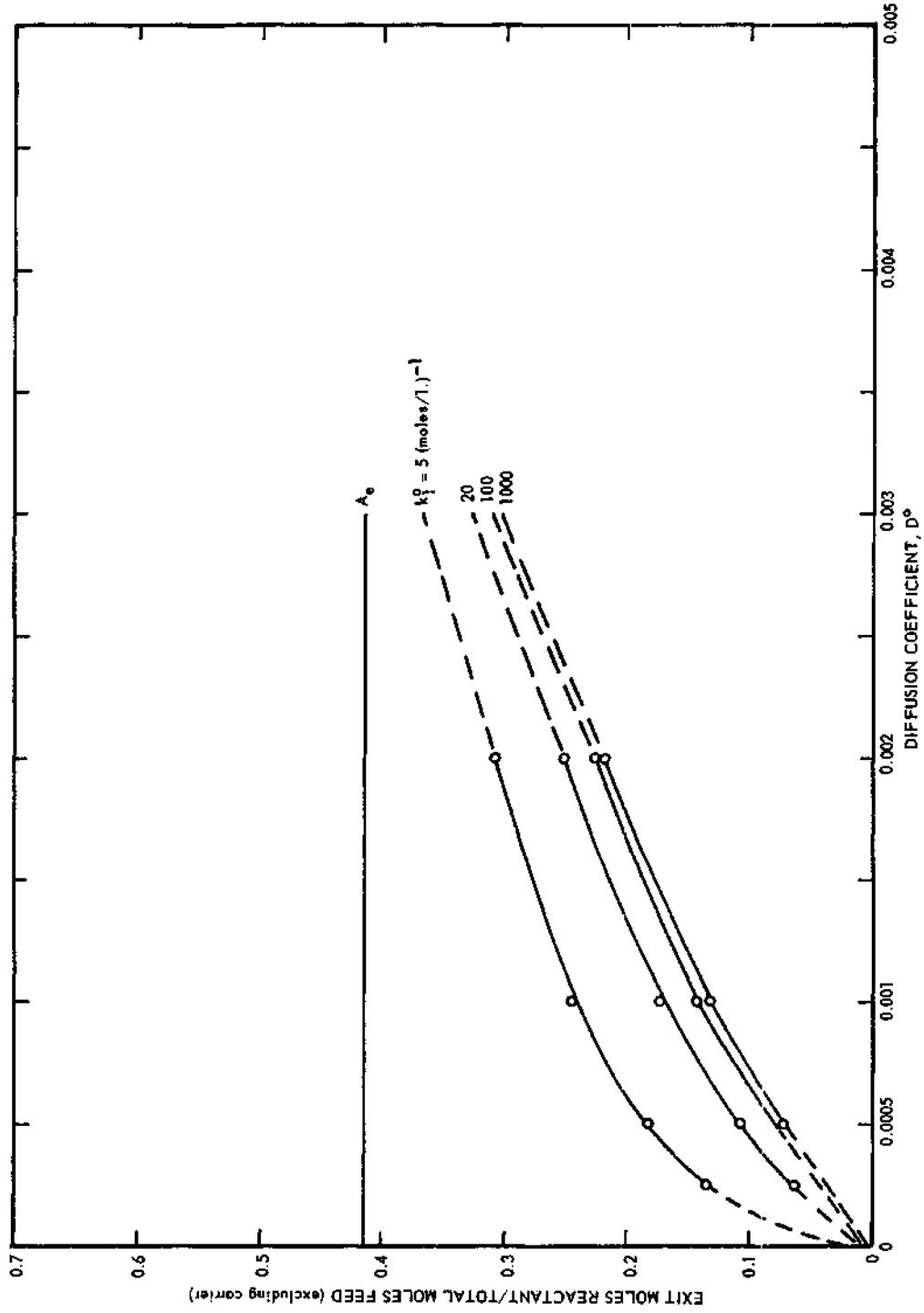

Figure 13. Effect of the Diffusion Coefficient on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Peak Emergence Time, T_R^o: 0.10.

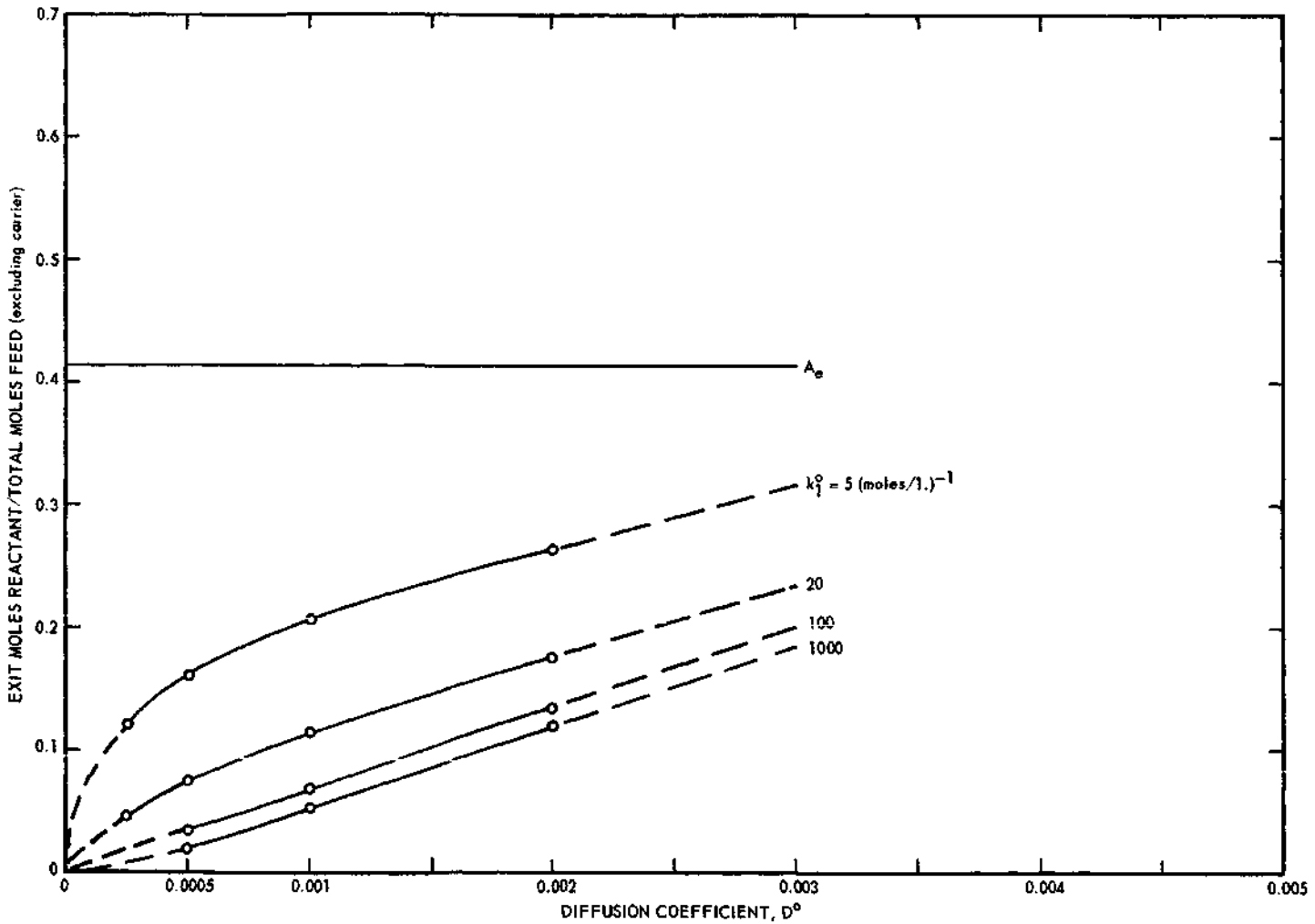

Figure 14. Effect of the Diffusion Coefficient on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Peak Emergence Time, T_R°: 0.15.

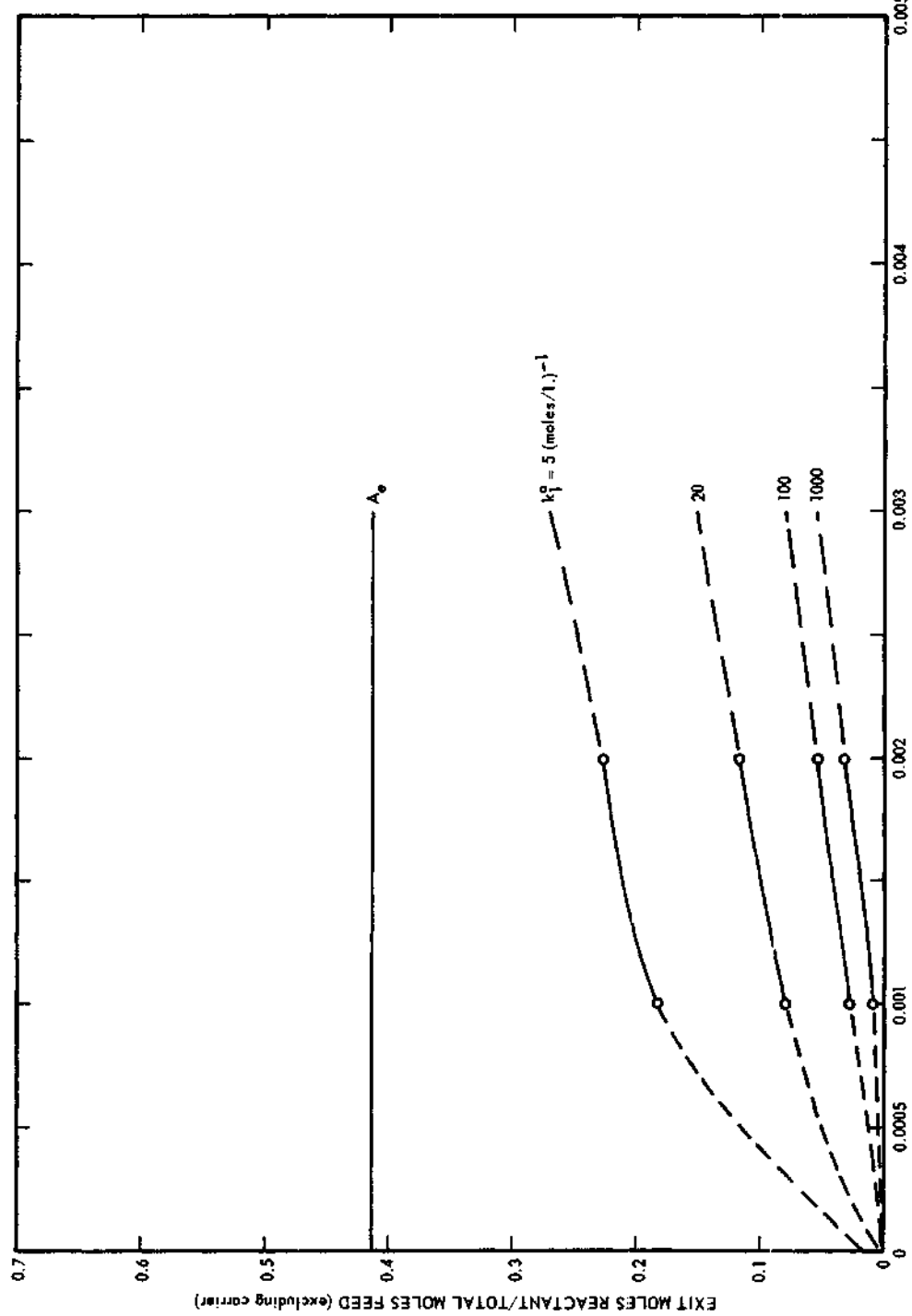

Figure 15. Effect of the Diffusion Coefficient on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Peak Emergence Time, T_R^o: 0.25.

component A decreases more rapidly for the smaller reaction rate constants than for the larger values.

For the larger reaction rate constants the amount reactant remaining decreases almost linearly with a decreasing diffusion coefficient over a considerable diffusion coefficient range. Again it is apparent that large reactant rate constants offer little improvement in the amount of reactant converted in a chromatographic reactor.

Effect of Reaction Rate Constants

The effect of the reaction rate constants on the amount of reactant remaining after passage through the chromatographic reactor is shown in Figures 16, 17, and 18 for reduced effective diffusion coefficients of 0.002, 0.001, and 0.0005, respectively. Calculations were made using four component peak separations and seven reduced reaction rate constants. With an equilibrium constant of 0.500, the reduced forward reaction rate constants were 2, 5, 20, 50, 100, 200, and 1000 $(\text{moles/l.})^{-1}$.

For all values of separations and diffusion coefficients, the amount of reactant at the chromatographic reactor exit decreases rapidly with increasing forward reaction rate constant. This reactant conversion increases very slowly for reduced reaction rate constants, k_1^o, greater than 50 $(\text{moles/l.})^{-1}$. Very little improvement is noticed with reduced rate constants of 100, 200, and 1000 $(\text{moles/l.})^{-1}$.

A comparison of Figures 16, 17 and 18 at different chromatogram peak separations further demonstrates the great improvement possible using a chromatographic reactor over a batch reactor. With a reduced

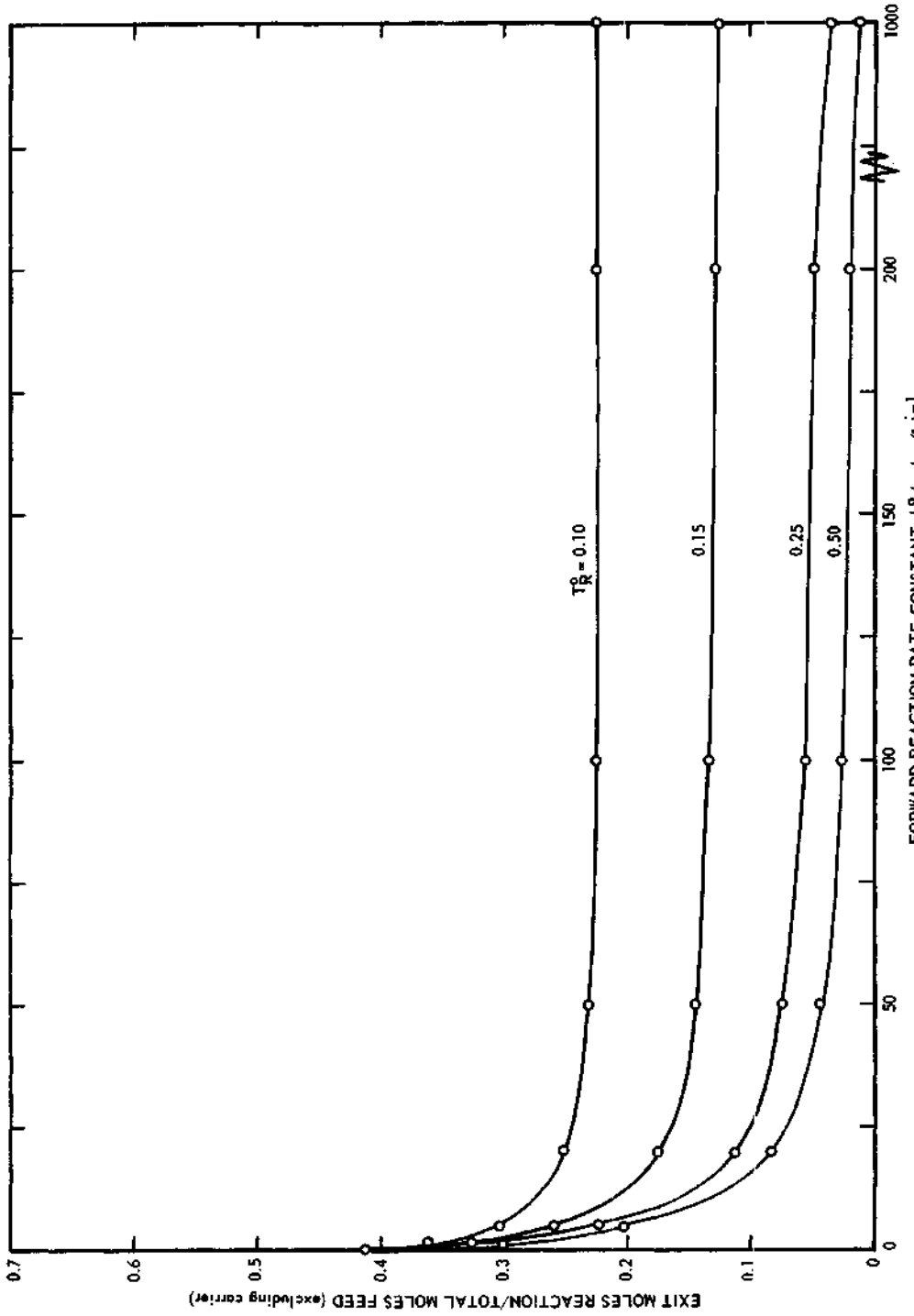

Figure 16. Effect of the Reaction Rate Constant on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Effective Diffusion Coefficient: 0.002

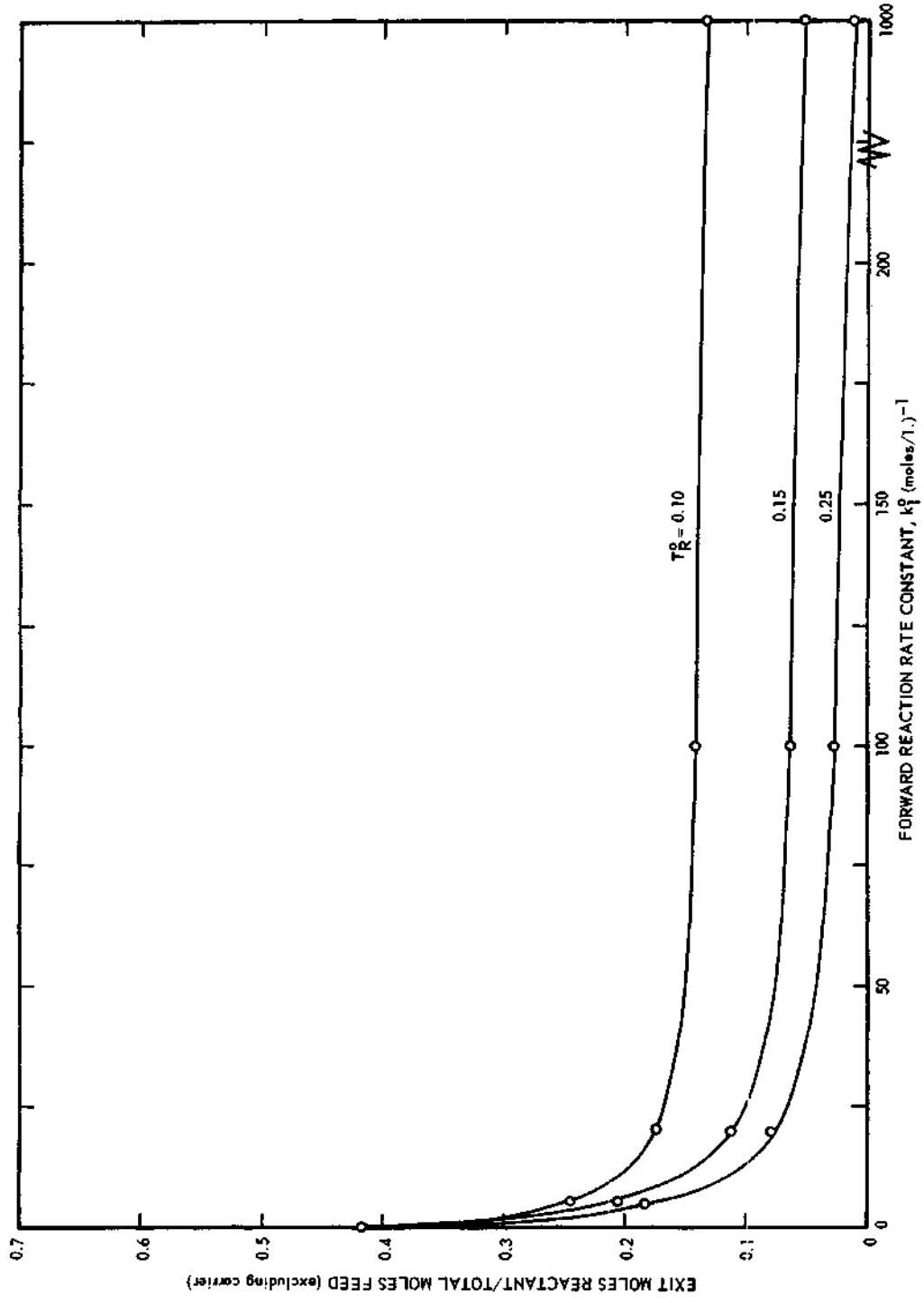

Figure 17. Effect of the Reaction Rate Constant on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Effective Diffusion Coefficient: 0.001.

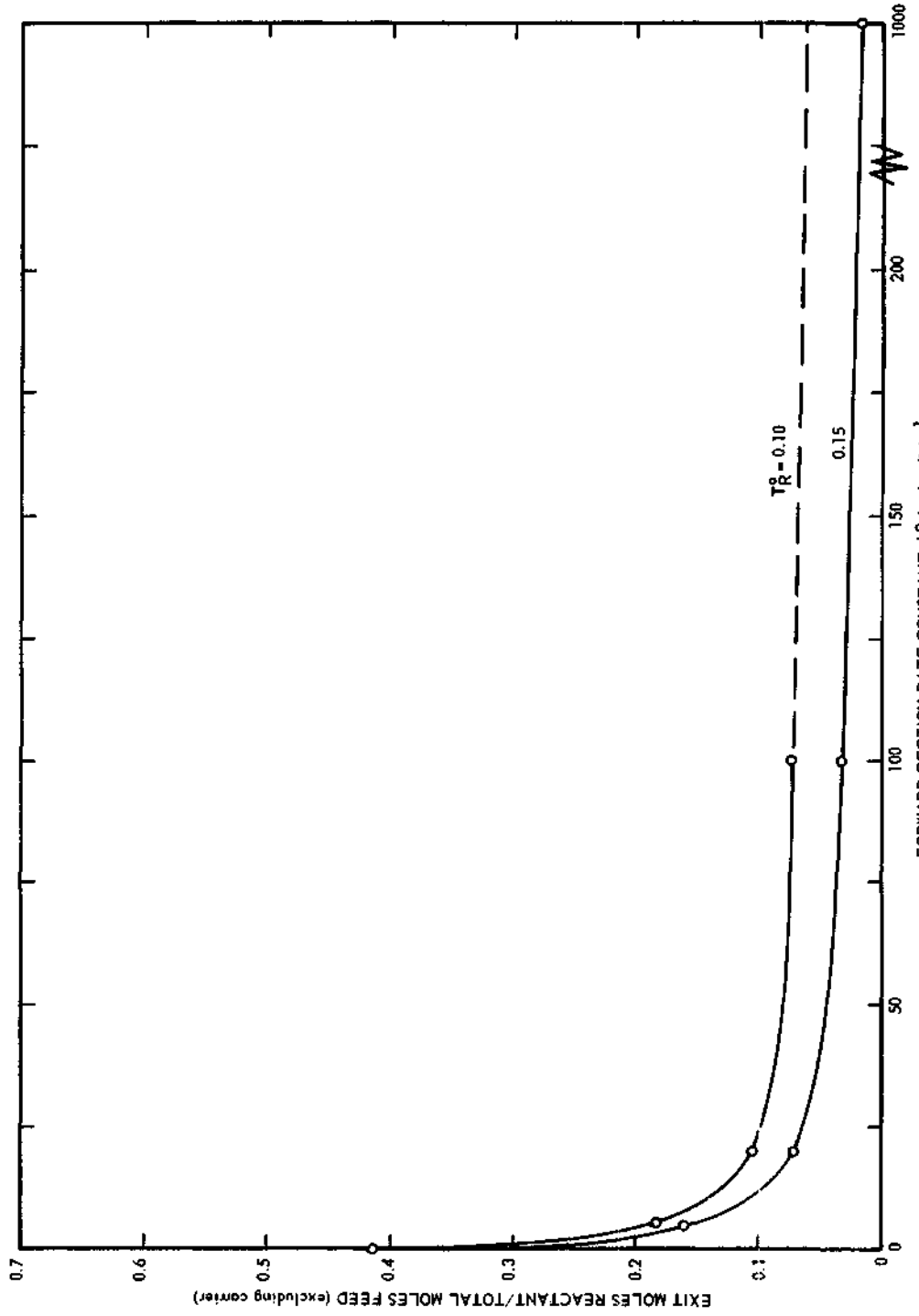

Figure 18. Effect of the Reaction Rate Constant on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Effective Diffusion Coefficient: 0.0005.

effective diffusion coefficient of 0.0005* and the small peak separation, T_R^o, of 0.15, reactant A has been reduced from an initial mole fraction of 0.414 to less than 0.020. This amount is less than five percent of the batch equilibrium value and represents a 20 fold improvement in reduction of the remaining reactant.

The use of reduced reaction rate constants may remove their physical significance. In order to provide some meaning to the magnitude of the reduced rate constants, calculations were performed for a batch reactor with a non-equilibrated feed. For an initial equal molar mixture of A, B and C and a total molar concentration of 10 moles/l., Figure 19 presents a graph of the mole fraction of component A versus the reduced time, T. It should be remembered that component A emerges from the chromatographic reactor at a reduced time of 1.00. If the actual retention time of component A is 10 minutes, the maximum reduced time, T, shown in Figure 19 corresponds to only three seconds. A reduced forward reaction rate constant of 1000 $(\text{moles/l.})^{-1}$ would give a mixture essentially at equilibrium in less than one-half second. Obviously with such a rapid reaction, calculations made at this high rate constant can be considered equivalent to instantaneous reaction equilibrium.

Effect of Non-Equilibrated Feed

Most of the calculations were made using an equilibrated feed

*Systems with low reduced diffusion coefficients of 0.0005 may be found. In the experimental section of this investigation reduced effective diffusion coefficients between 0.0003 and 0.0006 were quite common.

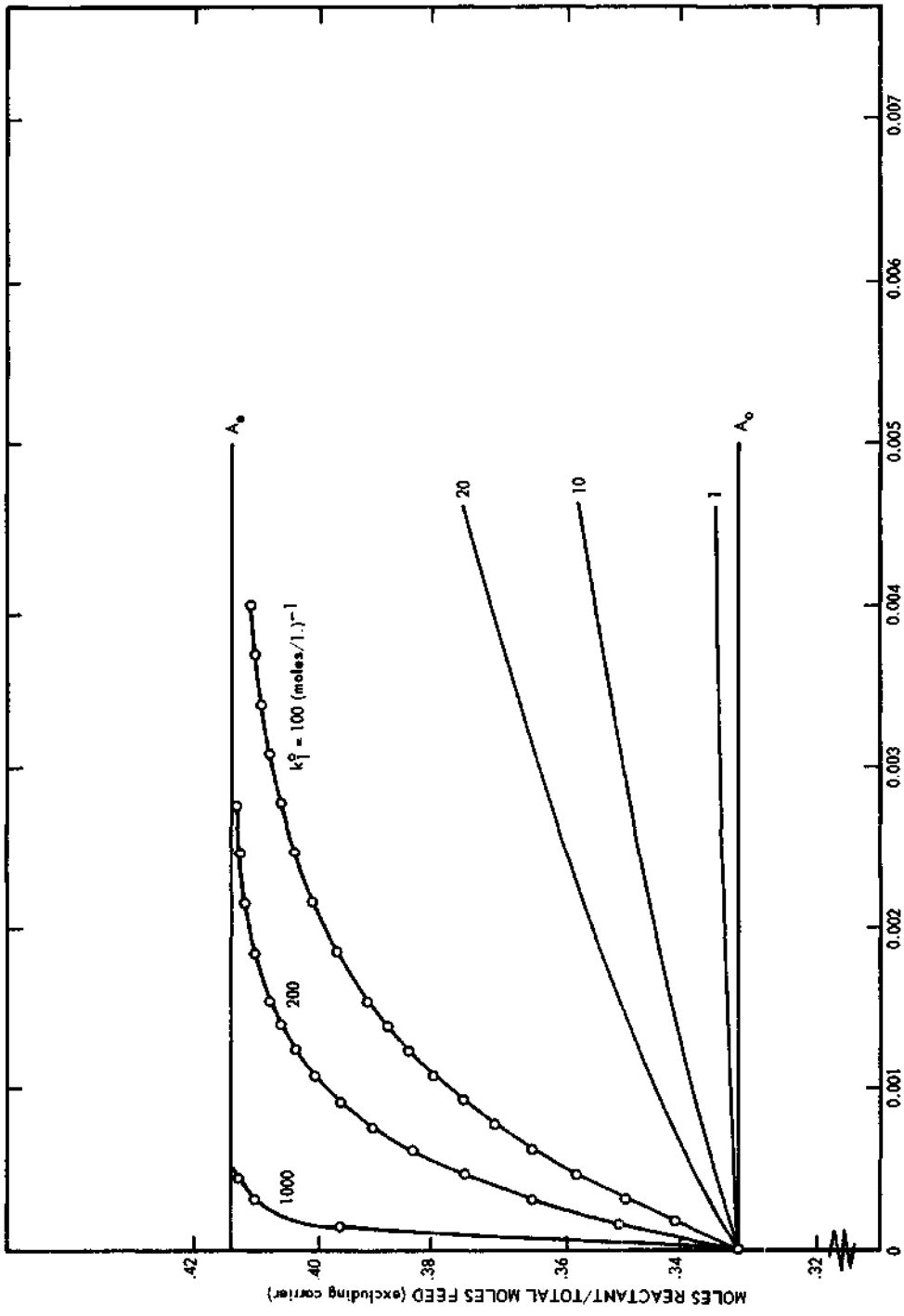

Figure 19. Equilibrium Convergence of Batch Reaction as a Function of the Forward Reaction Rate Constant.
Equilibrium Constant: 0.500.

to the chromatographic reactor. This choice was made to insure that any decrease in reactant was due entirely to the chromatographic reactor concept and did not include a change that could have been obtained in a batch or continuous reactor. To determine the effect of using pure reactant A (rather than an equilibrium mixture of A, B and C) a series of calculations were made at three separations, T_R^o, with a reduced effective diffusion coefficient equal to 0.002. The results are presented in Figure 20. A comparison with Figure 16 reveals no significant difference for a reduced forward reaction rate constant greater than 20 $(\text{moles/l.})^{-1}$. However, for reduced rate constants less than 3.0 $(\text{moles/l.})^{-1}$ the exit mole fraction of A is greater than the minimum obtainable using a static equilibrium system rather than a chromatographic reactor. For small reaction rate constants an equilibrated feed should always be used.

Effect of the Equilibrium Constant

Most of the numerical solutions were obtained with an equilibrium constant of 0.500. This value was chosen because the equilibrium constant at 77° K. for the $2HD \rightleftarrows H_2 + D_2$ reaction is 0.526 (31). The equilibrium constant was assumed to be the ratio of the forward reaction rate constant divided by the reverse reaction rate constant.

If the equilibrium constant is larger than unity, a chromatographic reactor would offer only a small improvement over that obtained in a batch or continuous tubular reactor. For example, an equilibrium mixture of H_2-HD-D_2, with equal molar concentrations of H_2 and D_2, would contain a HD mole fraction of 0.200, 0.137, 0.0909, and 0.0576

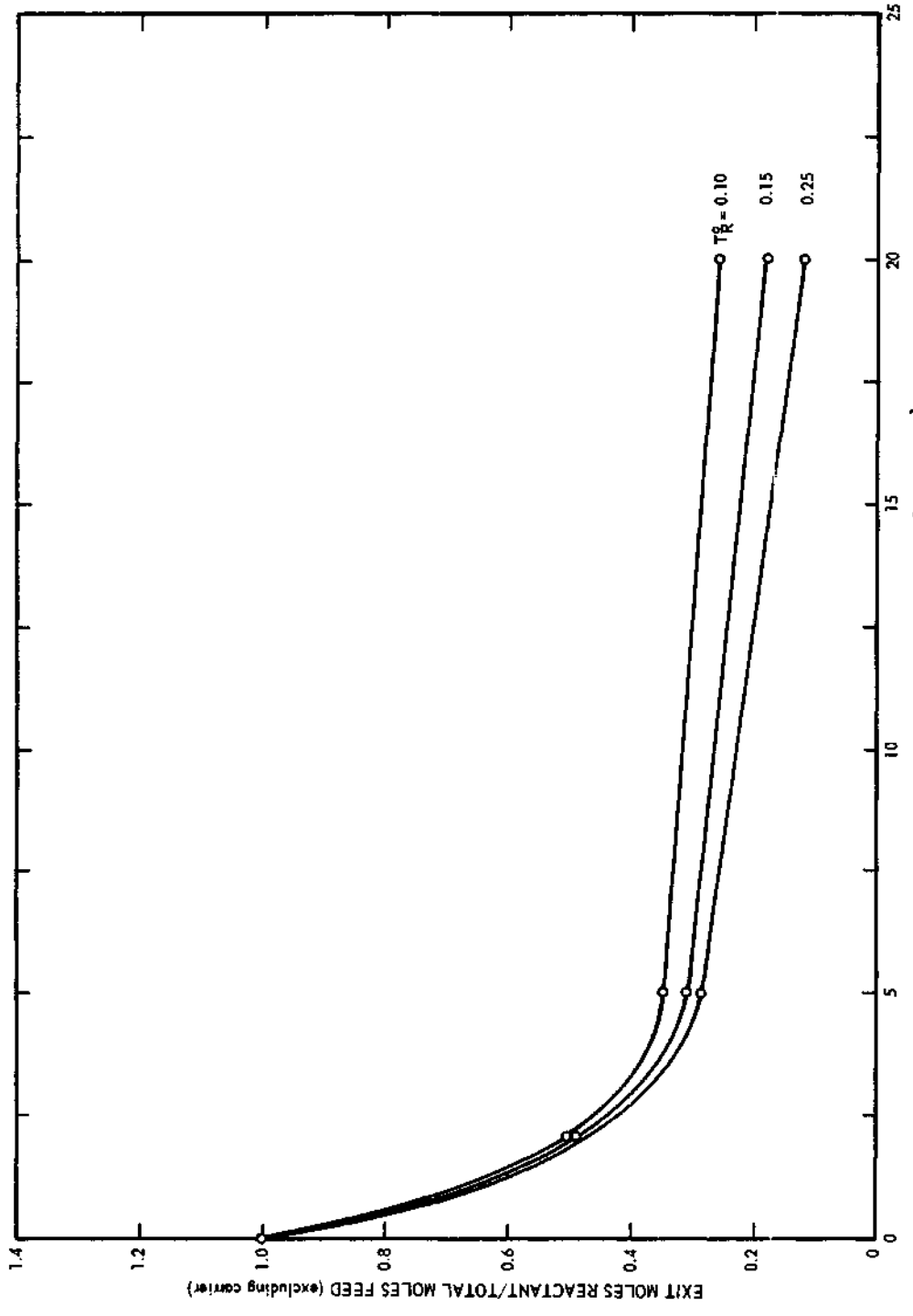

Figure 20. Effect of a Non-Equilibrated Reactant on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Effective Diffusion Coefficient: 0.002.

for equilibrium constants of 4, 10, 25, and 100 respectively. There appears little need of the chromatographic reactor concept for large equilibrium constants.

The unique feature of the chromatographic reactor is its ability to give yields for reversible reactions greater than the maximum possible with a batch or continuous tubular reactor (even under conditions of instantaneous equilibrium). The amount of reactant A remaining was calculated as a function of the equilibrium constant to determine the range of equilibrium constants of interest. An equilibrium constant, K_e, of 1.00 was taken as the maximum value for the previously outlined reasons. Magee (16) had suggested a minimum equilibrium constant of 2×10^{-7}. However, this suggestion was based on a chromatographic reactor model that neglected diffusion and assumed instantaneous equilibrium. Probably a much larger value would be more realistic.

Figure 21 shows the equilibrium constant effect on the amount of reactant remaining at a reduced peak emergence time, T_R^o, of 0.15 and a reduced effective diffusion coefficient of 0.002. All calculations were made using an equilibrium feed mixture of A, B and C with $B_o = C_o$. The exit mole fraction of reactant A is shown as a function of the reduced reverse reaction rate constant, k_2^o. It should be remembered that the reduced forward reaction rate constant is $k_1^o = k_2^o (K_e)$.

Only a marginal improvement appears possible using the chromatographic reactor with reactions having an equilibrium constant less than 0.001. For $K_e = 0.001$ the chromatographic reactor can reduce the amount of reactant remaining after equilibrating in a batch reactor

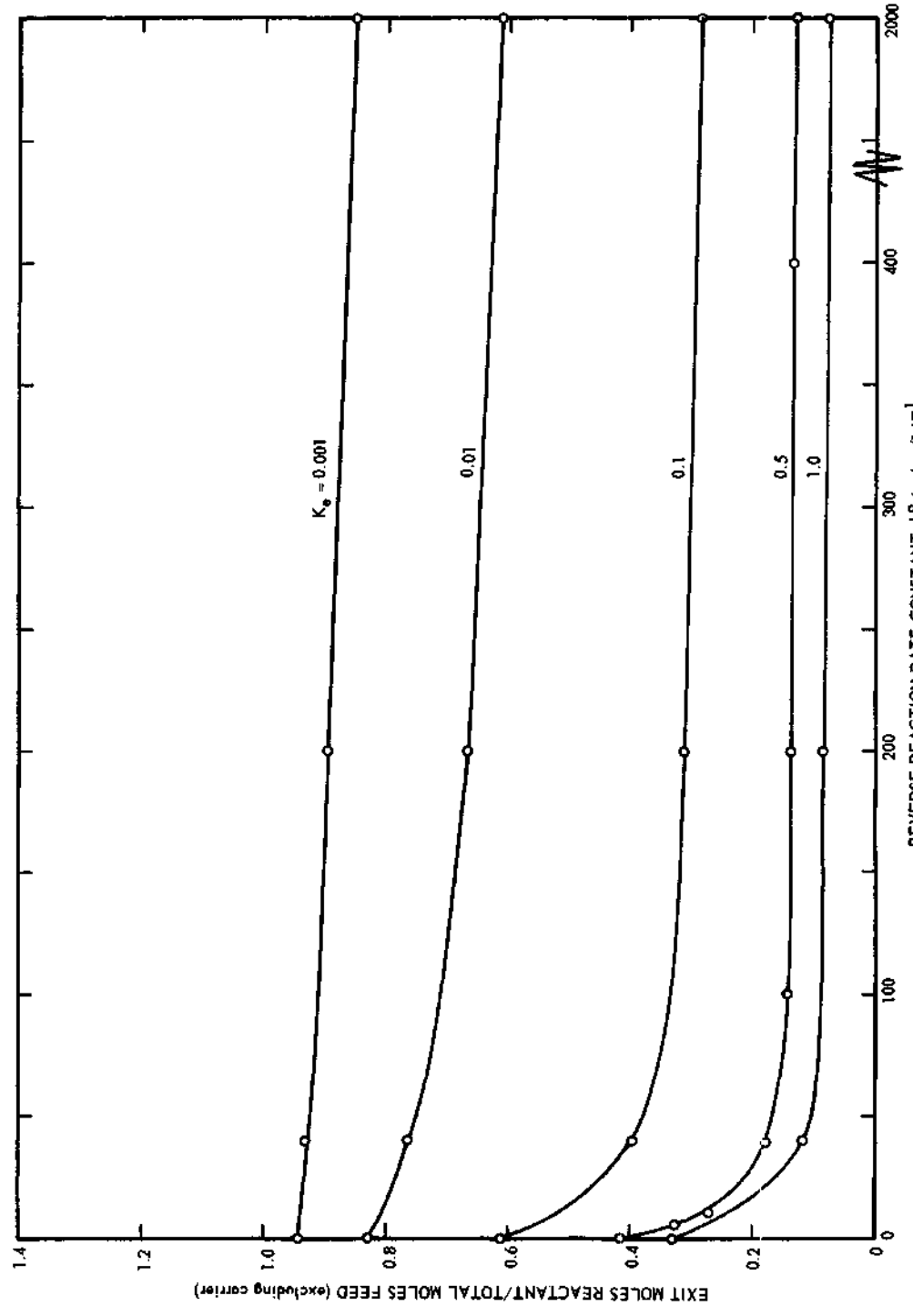

Figure 21. Effect of the Equilibrium Constant on the Amount of Reactant Remaining.
Reduced Effective Diffusion Coefficient: 0.002.
Reduced Peak Emergence Time: 0.15.

from about 94 percent to less than 86 percent with a reduced reverse reaction rate constant, k_2^o, of 2000 $(moles/l.)^{-1}$. This improvement amounts to only a 8.5 percent reactant reduction.

It might be argued that the minimum limit for the equilibrium constant should be determined from a study of the yield versus the reduced forward reaction rate constant, k_1^o. For example, comparison at a reduced reverse reaction rate constant of 2000 $(moles/l.)^{-1}$, the reduced forward reaction rate constant, k_1^o, with $K_e = 0.001$ is only 2.0 $(moles/l.)^{-1}$, while with $K_e = 0.01$, $k_1^o = 20$ $(moles/l.)^{-1}$. It could be argued that with a reduced forward reaction rate constant equal to 20 $(moles/l.)^{-1}$ the reaction with the equilibrium constant equal to 0.001 might give almost equal results compared to an equilibrium constant of 0.01. However, remembering that $k_1^o = k_2^o (K_e)$, Figure 21 gives an exit mole fraction A of about 0.85 at $K_e = 0.001$ and $k_1^o = 2.0$ $(moles/l.)^{-1}$, in contrast to an exit mole fraction of 0.66 for $K_e = 0.01$ and $k_1^o = 2.0$ $(moles/l.)^{-1}$. Even calculated as a percentage of the batch equilibrium mole fraction, it is obvious that there is a greater reduction with $K_e = 0.01$ than $K_e = .001$. This conclusion should be expected because as the equilibrium constant is reduced holding the forward reaction constant fixed, the reverse reaction rate constant must increase and further hinder the desired reaction.

Russian workers (4,13,14,15) have proposed chromatographic reactor models using the assumption that reversible reactions occurring during separation are irreversible. This neglect of the reverse reaction was taken to be true because the products were continuously

separating and could not react in the reverse direction once separated. As discussed in Chapter I, this assumption is not realistic. It should be noted that this assumption would be more valid if the equilibrium constant was much larger than unity. The reverse reaction rate constant would then be small compared to the forward rate constant and probably could be ignored. However, the previous discussion noted that there is little practical reason to use a chromatographic reactor with reactions having a large equilibrium constant. In the range of interest the reverse rate constant is larger than the forward rate constant.

To test the magnitude of the error caused by using the irreversible reaction assumption, two numerical calculations were made at a reduced effective diffusion coefficient of 0.002 and a peak separation, T_R^o, of 0.15. At a reduced forward reaction rate constant, k_1^o, of 20 $(\text{moles/l.})^{-1}$, the exit mole fraction of reactant A was decreased from an equilibrium of 0.414 to 0.0792. The inclusion of a reduced reverse reaction rate constant, k_2^o, of 40 $(\text{moles/l.})^{-1}$ only reduced the reactant to a mole fraction of 0.175. Obviously the irreversible reaction assumption is not realistic and gives an excessive reduction compared to including the reverse reaction.

At a reduced forward reaction rate constant equal to 100 $(\text{moles/l.})^{-1}$, the results are even more erroneous. Neglecting the reverse reaction gives an exit mole fraction of reactant A of 0.0195. With a reverse reaction, the mole fraction of reactant A is reduced to 0.132. The assumption that a reversible reaction proceeds irreversibly in a chromatographic reactor is quite limiting and would appear much worse at lower equilibrium constants.

Effect of the Peak Emergence Order

All the previous numerical solutions were obtained using component velocities fixed relative to R_a^o such that $R_c^o > R_a^o > R_b^o$. This choice gives the optimum peak emergence order for the reaction $2A \rightleftarrows B + C$. Reactant A travels through the chromatographic reactor between components B and C. As component C is formed, it separates from reactant A because $R_c^o > R_a^o$. Likewise, any component B produced has a slower column velocity than reactant A and separation results. The products are always separating from each other and move toward a lower concentration region of the other product. There is no time during which one product moves into a higher concentration region of the other product. This choice of the relative component column velocities gives the minimum chance for occurrence of the reverse reaction.

Two other unique choices of the peak emergence order exist. These peak orders are $R_a^o > R_b^o > R_c^o$ and $R_c^o > R_b^o > R_a^o$. With both peak emergence orders, any product C produced from reactant A by the reaction $2A \rightleftarrows B + C$ must pass through a relatively high concentration region of product B. The time during which there is a possibility of the reverse reaction occurring is greatly increased and a lower conversion of reactant A should be expected.

Calculations were performed at all three peak emergence orders to determine the amount of reactant A converted. A reduced effective diffusion coefficient of 0.002 and an equilibrium constant of 0.500 were used. For all calculations the reduced column velocity of component A was held constant at $R_a^o = 1.00$. The values of the other column

velocities were taken such that all component peaks on a non-reactive chromatogram would be separated by a reduced time, $\bar{t}$, of 0.15. For the column velocity order $R_a^o > R_b^o > R_c^o$, the retention times used were $T_{Ra}^o = 1.00$, $T_{Rb}^o = 1.15$, and $T_{Rc}^o = 1.30$. For $R_c^o > R_b^o > R_a^o$, the retention times were $T_{Rc}^o = 0.70$, $T_{Rb}^o = 0.85$, and $T_{Ra}^o = 1.00$.

The effect of the peak emergence order is given in Figure 22 as a function of the reduced forward reaction rate constant, k_1^o. It is apparent that the successful use of a chromatographic reactor is only possible with the proper peak emergence order.

The difference in the amount of reactant remaining for two component velocity orders $R_a^o > R_b^o > R_c^o$ and $R_c^o > R_b^o > R_a^o$ is significant. For $R_a^o > R_b^o > R_c^o$, products B and C remain for a time in the chromatographic reactor after reactant A has completely emerged. A reverse reaction between B and C can occur to produce A and limit the amount of A converted. Although any A produced can react to form B and C, the concentration of A present is quite weak compared to the concentrations of B and C. This concentration difference results in a large conversion of B and C by the reverse reaction to produce component A.

With the component column velocity order $R_c^o > R_b^o > R_a^o$, products B and C emerge from the column before reactant A. There is much less time to produce component A by the reverse reaction. In this case an intermediate conversion is experienced relative to the other two peak emergence orders.

It is evident that the optimum component column velocity order should be used in a chromatographic reactor. This does not necessarily

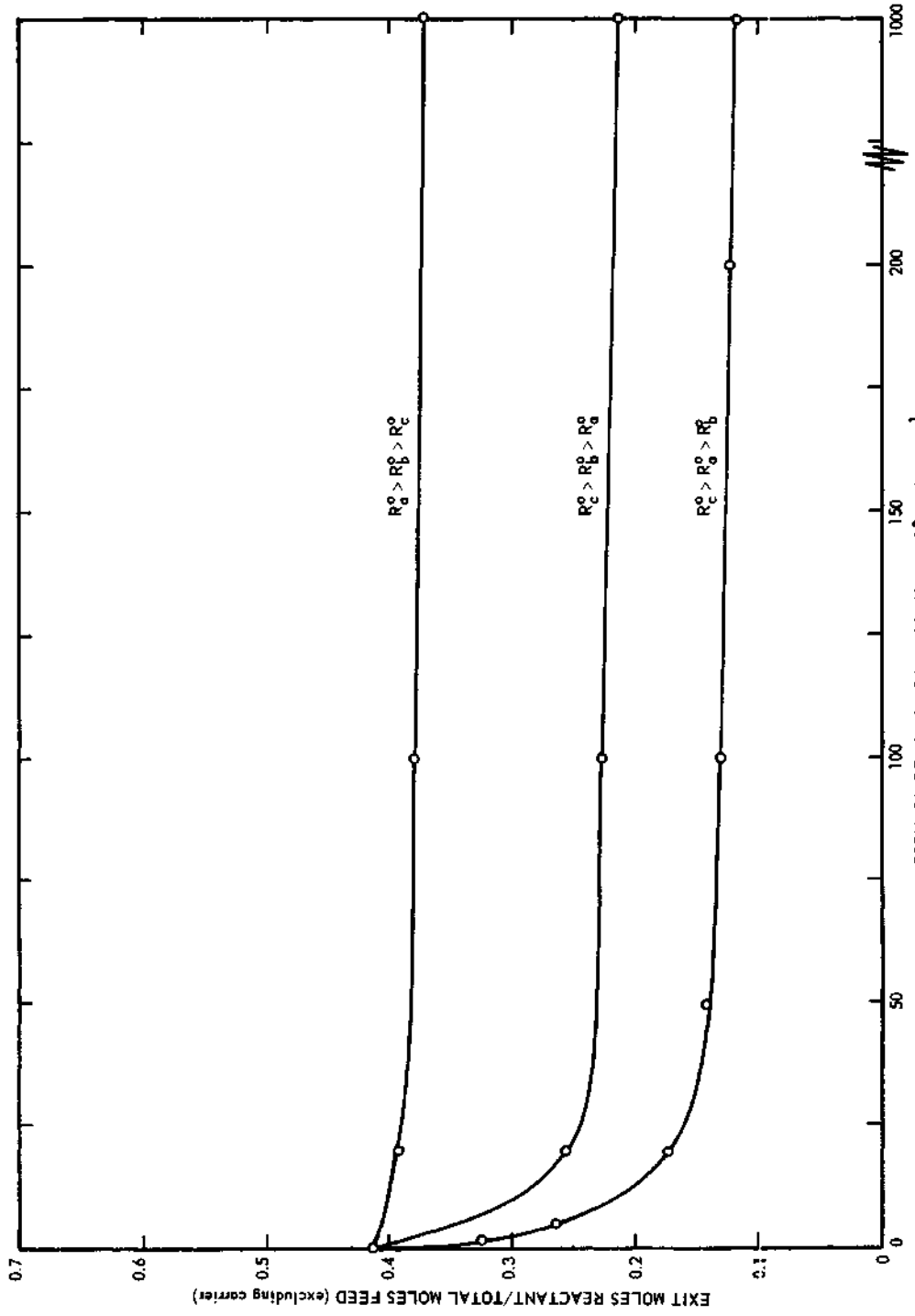

Figure 22. Effect of the Peak Emergence Order on the Amount of Reactant Remaining.
Reduced Effective Diffusion Coefficient: 0.002.
Equilibrium Constant: 0.500.

limit the application of a chromatographic reactor to a small number of reactions. A judicious choice of one of the many partitioning agents available can permit use of the optimum peak emergence order for almost any group of three components.

Bethune and Kegeles (12) discussed the effect of the three possible peak emergence orders in their theoretical study of the reaction A $\rightleftharpoons$ B + C which occurred during an extraction on a Craig machine. The authors showed that regardless of the relative velocity assigned to component A the maximum column concentration must lie between the maximum concentrations of B and C. Also it was noted that under these conditions it was possible for a component to have more than one concentration peak.

The model used by Bethune and Kegeles assumed instantaneous equilibrium. Results of this investigation, which considers finite reaction rates, show this effect to hold only at relatively high reduced forward reaction rate constants (greater than or equal to k_1^o = 100 $(\text{moles/l.})^{-1}$). For reduced forward reaction rates of 20 $(\text{moles/l.})^{-1}$ or less the maximum component concentrations exist in the same order as their assigned column velocities.

At a reduced forward reaction rate constant, k_1^o, of 1000 $(\text{moles/l.})^{-1}$ and the peak emergence order $R_a^o > R_b^o > R_c^o$, two concentration peaks were found in this investigation for component C. Between these peaks, the concentration of component C was only slightly less than the peak concentrations.

Effect of Feed Concentration

The numerical results of this investigation were calculated using an arbitrary total molar concentration for the feed of 10.0 moles/l. This value was used to facilitate the computation of the numerical solution scheme without requiring excessive values of the reduced reaction rate constants.

Four calculations were made to illustrate the effect of the total feed concentration on the amount of reactant remaining. An equilibrated feed (with $B_o = C_o$ and an equilibrium constant of 0.500) was used for the numerical solutions with total molar concentrations, $A_o + B_o + C_o$, equal to 0.1, 1.0, 5.0, and 10.0 moles/l. The results are shown in Figure 23 for a reduced effective diffusion coefficient, D_i^o, of 0.001, a reduced forward reaction rate constant, k_1^o, of 20 $(\text{moles/l.})^{-1}$, and a reduced peak emergence time, T_R^o, equal to 0.10.

The amount of reactant remaining decreases rapidly with increasing total molar concentrations less than 1.0 moles/l. However, as the total feed concentration increases further there is less and less reduction in the amount of reactant remaining after emerging from the chromatographic reactor. There appears to be a limit to the reduction possible with highly concentrated feeds. The results of this investigation indicate that the most important limiting process is diffusion.

Molar gas concentrations of 0.10, 1.0, 5.0, and 10.0 moles/l. correspond to approximate pressures of 2.5, 25, 125, and 250 atmospheres, respectively. Equipment design and construction would also limit the use at higher pressures. Probably most chromatographic reactor applications

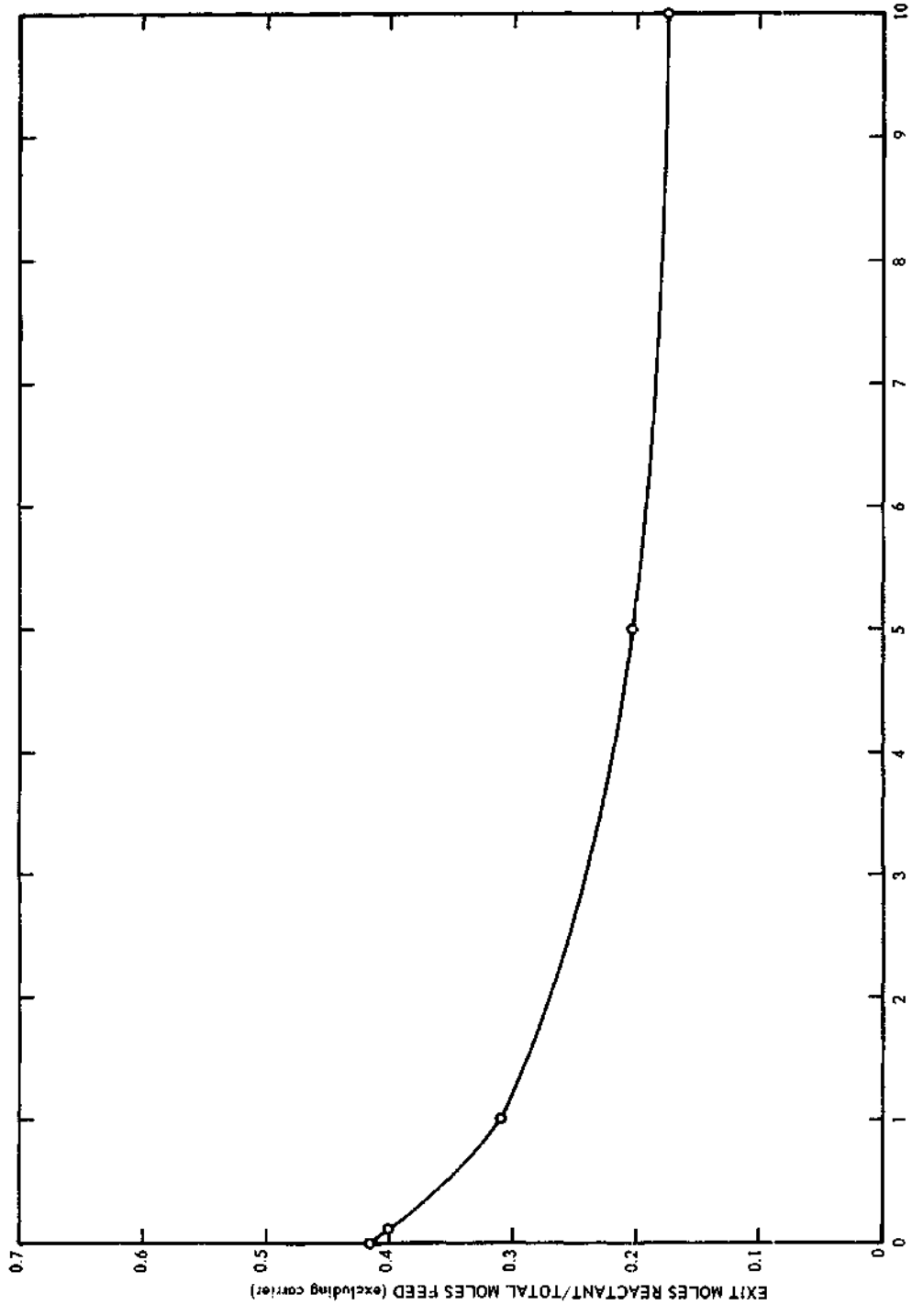

Figure 23. Effect of the Feed Concentration on the Amount of Reactant Remaining.
Equilibrium Constant: 0.500.
Reduced Effective Diffusion Coefficient: 0.001.
Reduced Peak Emergence Time: 0.10.

would offer sufficient reduction of reactant A over that possible in an equilibrium batch reactor at a total molar concentration in excess of one.

Although no calculations were made to determine the feed concentration effect for larger reaction rate constants, it is expected that lower total feed concentrations could be used with the larger reaction rate constants to achieve the same total conversion.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions have been drawn from the results of this investigation.

1. Neglecting the effects of diffusion and finite reaction rate constants results in a model of the chromatographic reactor that is not realistic. Predictions based on such a model at best can only indicate trends.

2. Calculations using the assumption that reversible reactions proceed irreversibly in a chromatographic reactor give excessive reactant conversions, especially for high reaction rate constants and low equilibrium constants.

3. The numerical scheme developed in this work gives an accurate, efficient computer solution of the nonlinear parabolic equations (5), (6), and (7) which describe the chromatographic reactor.

4. The chromatographic reactor has been shown to be capable of giving reactant conversions in excess of the maximum possible with a batch or tubular reactor. Under certain circumstances, essentially complete reactant conversion is possible accompanied by fully separated products.

5. The effective diffusion coefficients of the reactant and products have been shown to be a major factor limiting conversion in a chromatographic reactor.

6. Reactant conversions significantly in excess of the static equilibrium values can be obtained with reversible reactions whose equilibrium constants are equal to or greater than 0.001.

7. Large chromatographic separations of components are unnecessary and result in only marginal further reactant conversion over that possible with moderate separations. Relative retention ratios between adjacent components in the chromatographic reactor of less than 1.25 are sufficient, and adequate conversion is possible with retention ratios as small as 1.01 - 1.05.

8. Large reaction rate constants offer small improvements and do not appear to be a major factor controlling the conversion.

9. The feed to the chromatographic reactor should be an equilibrium mixture of the reactant and products to insure maximum conversion.

10. High feed concentrations should be used; however, excessive feed concentrations offer little conversion improvement.

11. The reactant should pass through the chromatographic reactor with a column velocity intermediate between the velocities of the two products to insure maximum reactant conversion.

The following recommendations for additional studies have been suggested from the results of this work.

1. The numerical solutions presented in this work should be extended to determine the effect of other than equal peak separations and equal diffusion coefficients.

2. Calculations should be performed to determine the effect of separation, diffusion, and reaction rate constants on conversion with reactions having equilibrium constants between 0.01 and 1.0.

3. Additional calculations should be made to determine the reactant conversion as a function of separation, diffusion, and reaction rate constants at lower total molar feed concentrations and larger sample volumes.

4. The numerical scheme offered for solution of the nonlinear equations describing the chromatographic reactor should be modified and used to study other possible reactions, such as $A \rightleftarrows B + C$ and $A + B \rightleftarrows C + D$.

5. Experimental data should be obtained for a reversible reaction in a chromatographic reactor, constructed to take advantage of the greater conversion at higher feed concentrations, and compared to the numerical solutions presented in this investigation.

APPENDICES

APPENDIX A

NUMERICAL METHODS

Development of Finite Difference Approximations

Finite difference approximations of derivatives are obtained by differentiating various interpolation formulas formed by a Taylor series expansion of the original function. Subsequent manipulations of these approximations result in numerous finite difference equations. The following development is based largely on the work of Lapidus (38).

Expanding the function $f(x)$ in a Taylor series about h gives

$$f(x+h) = f(x) + \frac{h}{1!} f'(x) + \frac{h^2}{2!} f''(x) + \ldots + R_n$$

where R_n is the sum of the remaining terms in the infinite series.

The definition of the following linear operators is

$$Ef(x) = f(x+h)$$

$$\Delta f(x) = f(x+h) - f(x)$$

$$\nabla f(x) = f(x) - f(x-h)$$

$$\delta f(x) = f\left(x + \frac{h}{2}\right) - f\left(x - \frac{h}{2}\right)$$

and

$$Df(x) = f'(x)$$

where E, Δ, ∇, δ and D are called the shift, forward difference, backward difference, central difference, and differential operators, respectively.

The Taylor series expansion in operator notation, is

$$Ef(x) = \left(1 + \frac{hD}{1!} + \frac{h^2D^2}{2!} + \ldots.\right) f(x)$$

Recognizing this expansion as the infinite series representation of e^{hD} gives

$$E = e^{hD}$$

The following operator relations are useful:

$$\Delta = e^{hD} - 1$$

$$\nabla = 1 - e^{-hD}$$

$$\delta = e^{\frac{1}{2}hD} - e^{-\frac{1}{2}hD} = 2\sinh\left(\tfrac{1}{2}hD\right)$$

Manipulation of these relations yields

$$hD = \log E = \log(1+\Delta) = -\log(1-\nabla) = 2\operatorname{arcsinh}\frac{\delta}{2}$$

Expansion of $hD = \log(1+\Delta)$ in a series approximation leads to

$$f'(x) = \frac{1}{h}\left(\Delta - \frac{\Delta^2}{2} + \frac{\Delta^3}{3} \ldots.\right) f(x)$$

Truncation of the series after the first difference gives

$$f'(x) = \frac{f(x+h) - f(x)}{h} + O(h) \qquad \text{(A-1)}$$

where $O(h)$ is the order of the truncation error.

Expansion and truncation after the first difference for

$$hD = 2 \operatorname{arcsinh} \frac{\delta}{2}$$

yields

$$f'(x) = \frac{f(x+h) - f(x-h)}{2h} + O(h^2) \qquad \text{(A-2)}$$

Similar expansion and truncation of

$$h^2D^2 = \left(2 \operatorname{arcsinh} \frac{\delta}{2}\right)^2$$

results in

$$f''(x) = \frac{f(x+h) - 2f(x) + f(x-h)}{h^2} + O(h^2) \qquad \text{(A-3)}$$

Other finite difference approximations can be obtained from the remaining operator relations or from truncation of the previous equations after higher differences.

Finite Difference Approximations of Partial Derivatives

Let the function $f(x,t)$ be defined on the x-t plane bounded by $-\infty < x < \infty$ and $0 \leq t < \infty$. A rectangular grid may be placed over the region of interest in the x-t plane with an h-interval spacing in the x direction and a k-interval spacing in the t direction. The grid mesh points are defined by the relation

$$f_{i,j} = f(ih,jk) = f(x_i,t_j)$$

where i and j are integers and j is non-negative.

Using Equations (A-2) and (A-3), the finite difference approximations of the partial space derivatives can be written as,

$$\frac{\partial f_{i,j}}{\partial x} = \frac{1}{2h} (f_{i+1,j} - f_{i-1,j}) + O(h^2) \qquad \text{(A-4)}$$

and

$$\frac{\partial^2 f_{i,j}}{\partial x^2} = \frac{1}{h^2} (f_{i+1,j} - 2f_{i,j} + f_{i-1,j}) + O(h^2) \qquad \text{(A-5)}$$

A similar equation for the time derivative using Equation (A-1) gives

$$\frac{\partial f_{i,j}}{\partial t} = \frac{1}{k} (f_{i,j+1} - f_{i,j}) + O(k) \qquad \text{(A-6)}$$

Finite Difference Approximations of Parabolic Equations

The choice of finite difference approximations used in a numerical solution is not entirely optional. There are many difference equations which will yield a solution of the desired partial differential equation. There is no one best approximation scheme for any given equation and its associated boundary conditions. However, the selection of several schemes can be made which will facilitate a more rapid and accurate calculation. This selection is made after a careful review of the effect of stability, convergence, and truncation error on the effort required for a solution.

Equations (5), (6) and (7) and the associated boundary conditions follow from the mathematical model of the chromatographic reactor. These equations are nonlinear parabolic differential equations. The classical one-dimensional heat or diffusion equation is a limiting form of the

parabolic type, whose solutions have been extensively investigated.

Explicit techniques represent the simplest and most straightforward finite difference schemes. The second space derivative of the diffusion equation is replaced by the appropriate approximation on the grid row corresponding to t = 0. All the mesh points on this row are known and represent the initial conditions. The time derivative is approximated between the initial time row and the second time row. All of the values on the second row can be readily calculated using the initial values.

The computation scheme extension consists of calculating explicitly all the mesh points on the third row, using the previously calculated second row values. This procedure is continued until all grid points are known for sufficiently large times.

Several convenient features are available using an explicit difference equation. First, each point to be calculated is simply related to three known grid points, yielding an explicit equation in one unknown for each new mesh point. Second, only a simple digital computation program is required, with minimum storage requirements.

There are severe restrictions on the use of explicit approximations that limit their computer application. Richtmyer (39) noted that explicit equations require extensive computation time to achieve the desired accuracy whenever small distance increments are used. Explicit equations are conditionally stable, requiring

$$\frac{Dk}{h^2} \leq \frac{1}{2}$$

where D is the diffusion coefficient in the diffusion equation.

Implicit equations have no such stability requirement, being unconditionally stable for all values of h and k. There is no limit on the maximum time step associated with the distance step. As a result, larger time steps can be used requiring less computation time to reach a desired solution. However, the implicit computation scheme is more complicated than the explicit scheme and requires more computer storage. Primarily because of the unconditional stability (and the availability of high speed computers with large storage), most solutions of parabolic equations use implicit difference schemes. All further discussion will concern only implicit techniques.

Laasonen gave an example of a simple implicit scheme for the diffusion equation. A substitution of the finite difference relation (A-5) for the second space derivative was made on the grid row to be calculated. The time derivative approximation (A-6) was used between the desired row and the previously calculated row. For each new mesh point one implicit equation results, involving three unknown mesh points on the new row and only one known point on the previous row. If equations are written for all new mesh points, a system of simultaneous equations results with the same number of equations and unknowns. Solution of a matrix is required for every row calculated. However, the matrix is of a special form* (tridiagonal) allowing rapid solution and

*A reasonable requirement for any implicit difference equation is that it may involve no more than two time levels and three space levels. Such a prerequisite insures a tridiagonal matrix solution at each time step.

requiring minimum storage.

The stability and convergence properties of Laasonen's implicit scheme (commonly called a backward difference equation) have been extensively investigated for solutions of the diffusion equation. Douglas (40) and Wasow (41) have proved that the backward difference equation solution is unconditionally stable and converges to the partial differential solution as the grid mesh approaches zero.

The rate at which the difference equation solution converges to the parabolic equation solution can be discussed in terms of the order of the total truncation error of the difference equation. The total truncation error for the backward difference equation can be given as

$$O(k) + O(h^2)$$

Douglas (42) has studied the problem of obtaining a solution of the backward difference equation out to a given time, T, with the truncation error held less than some prescribed value. It was concluded that if the ratio

$$\frac{h}{(k)^{\alpha}} = \lambda$$

is considered constant for all α, the minimum work would be required when $\alpha = \frac{1}{2}$. Using this criteria, the time step, k, is proportional to the square of the distance step, h. The convergence rate can be expressed as

$$O(k) + O(h^2) = O(k)$$

Crank and Nicholson (43) achieved a total truncation error improvement by averaging the space derivatives over the desired grid row and the previously calculated row. The improved error of this scheme is

$$O(k^2) + O(h^2)$$

Douglas (40) proved the Crank-Nicholson system unconditionally stable. While the rate of convergence with a fixed ratio, $\lambda = k/h^2$ is given by

$$O(k^2) + O(h^2) = O(k)$$

the suggestion was made to modify the usual convergence criteria such that the fixed ratio, $R = k/h$ is held constant. This ratio is a logical choice since the total truncation error involves h and k in an equal manner. Using this fixed ratio, the finite difference solution converges to the differential solution with the rate given as

$$O(k^2) + O(h^2) = O(k^2)$$

Wasow (41) proved the convergence of the difference equation solution for any form of h and k approaching zero.

Various initial conditions and their effect on the convergence of the Crank-Nicholson procedure have been studied by Juncosa and Young (44). For step functions and linear functions as initial conditions, it was shown that the difference solution still converged at the rate, $O(h^2)$.

A further improvement in the total truncation order was suggested

by Douglas (40,45) and Richtmyer (39). In addition to the Crank-Nicholson average of the space derivatives, a weighted average of the time derivative was used which included mesh points on either side of the desired point. Douglas proved the unconditional stability of this procedure. The order of the truncation error for the implicit difference equation is

$$O(k^2) + O(h^4)$$

A convergence rate of

$$O(k^2) + O(h^4) = O(k^2)$$

was given, where the fixed ratio $\lambda = k/h^2$ was maintained as h and k approached zero. Douglas determined that this higher order scheme was slightly superior to the Crank-Nicholson procedure. While both methods have the same order of convergence rate, the time averaged method has a smaller coefficient, requiring fewer calculations for the same accuracy.

All of the previous implicit difference equations have involved only the linear diffusion equation. Richtmyer (39) has considered the effect of lower order terms on the stability of linear parabolic equations and found that implicit difference schemes are practically unaffected by the lower order terms.

The study of stability and convergence for nonlinear parabolic equations is difficult, if not impossible. Rose (46) and Lees (47) have proposed implicit difference techniques for solving general

nonlinear parabolic equations of the form

$$\frac{\partial}{\partial x}\left(p(x,t)\,\frac{\partial u}{\partial x}\right) = F\left(x,t,u,\frac{\partial u}{\partial x},\frac{\partial u}{\partial t}\right)$$

Implicit finite difference equations which approximate nonlinear parabolic equations are usually nonlinear and require iterative solution techniques. Lees has proposed a modified backward difference scheme that eliminates the reiteration requirement if

$$F\left(x,t,u,\frac{\partial u}{\partial x},\frac{\partial u}{\partial t}\right) = F_1\left(x,t,u,\frac{\partial u}{\partial x}\right) + F_2\left(x,t,u,\frac{\partial u}{\partial x}\right)\frac{\partial u}{\partial t}$$

The function u and its first space derivative are evaluated at time, (t - k), instead of the usual backward difference at time, t. All other derivatives are evaluated at time, t. This modification of the backward difference equation yields a linear matrix system of the tridiagonal type which gives a solution at each time level without reiteration.

Lees proved the order of the truncation error for the modified backward difference scheme to be

$$O(k) + O(h^2)$$

for all constant values of the mesh ratio $\lambda = k/h^2$. Therefore, the convergence rate is given as

$$O(k) + O(h^2) = O(k)$$

If the function $F\left(x,t,u,\frac{\partial u}{\partial x},\frac{\partial u}{\partial t}\right)$ is a nonlinear function of $\frac{\partial u}{\partial t}$, the modified difference equation must be solved using an iteration

technique. Lees developed an iterative procedure and proved that a unique difference solution exists, which converges to the differential solution for small h and k.

Rose (46) conceived a general weighted combination of the first and second space derivatives on the time rows t and (t - k). The approach was quite similar to the Crank-Nicholson difference equation, where the space derivatives are equally weighted. Rose showed that the reiterative solution of his difference equation converged to the differential solution with the rate given as

$$O(k) + O(h^2) = O(k)$$

for any constant value of $\lambda = k/h^2$.

Lees (47) extended the Crank-Nicholson difference method to include nonlinear parabolic equations. Instead of evaluating the function u at time, t, as Rose did, Lees used an average of the function at the time levels t and (t - k). This choice improved the convergence rate to

$$O(k^2) + O(h^2) = O(k)$$

for all values of the mesh ratio $\lambda = k/h^2$. While this convergence rate is of the same order as that for the scheme of Rose, the coefficient is smaller and a smaller error results.

It has been shown that stable finite difference solutions of nonlinear parabolic differential equations exist. Convergence of the difference solution to the differential solution has been proved for

sufficiently small h and k. This convergence holds regardless of whether an iterative solution technique is required. The truncation error and convergence rate have been included for all difference equations discussed.

Finite Difference Approximations of Chromatographic Reactor

The finite difference approximations in the present investigation represent a combination of the extended Crank-Nicholson procedure as due to Lees (47) and the weighted time derivative of Douglas (45) and Richtmyer (39). While no proof is offered, the previous papers would indicate a truncation error of

$$O(k^2) + O(h^4)$$

A convergence rate can be given as

$$O(k^2) + O(h^4) = O(k^2)$$

for any constant grid mesh ratio, $\lambda = k/h^2$.

The finite difference representations of the dependent variable, $A(X,T)$ and its derivatives are:

$$A(X,T) = \tfrac{1}{2}(A_{i,j+1} + A_{i,j}),$$

$$\frac{\partial A}{\partial X} = \frac{1}{4h}\left[(A_{i+1,j+1} - A_{i-1,j+1}) + (A_{i+1,j} - A_{i-1,j})\right],$$

$$\frac{\partial^2 A}{\partial X^2} = \frac{1}{2h^2}\left[(A_{i+1,j+1} - 2A_{i,j+1} + A_{i-1,j+1}) + (A_{i+1,j} - 2A_{i,j} + A_{i-1,j})\right],$$

$$\frac{\partial A}{\partial T} = \frac{1}{k}\left[\frac{1}{12}(A_{i-1,j+1} - A_{i-1,j}) + \frac{5}{6}(A_{i,j+1} - A_{i,j}) + \frac{1}{12}(A_{i+1,j+1} - A_{i+1,j})\right].$$

Similar expressions were written for the two dependent variables B(X,T) and C(X,T) and their derivatives.

Using these approximations, Equation (5) yields the following difference equation:

$$-\gamma_1 A_{i-1,j+1} + \gamma_2 A_{i,j+1} + \gamma_3 A_{i+1,j+1} = \gamma_4 A_{i-1,j} - \gamma_5 A_{i,j} - \gamma_6 A_{i+1,j} + \beta_1 \qquad \text{(A-7)}$$

with

$$\gamma_1 = 6kD_a^o + 3hkR_a^o - h^2,$$

$$\gamma_2 = 12kD_a^o + 10h^2 + 6h^2kk_1^o(A_{i,j+1} + A_{i,j}),$$

$$\gamma_3 = 3hkR_a^o - 6kD_a^o + h^2,$$

$$\gamma_4 = 6kD_a^o + 3hkR_a^o + h^2,$$

$$\gamma_5 = 12kD_a^o - 10h^2 + 6h^2kk_1^o(A_{i,j+1} + A_{i,j}),$$

$$\gamma_6 = 3hkR_a^o - 6kD_a^o - h^2,$$

$$\beta_1 = 6h^2kk_2^o(B_{i,j+1} + B_{i,j})(C_{i,j+1} + C_{i,j}).$$

The matrix coefficients γ_2, γ_5, and β_1 are not constants, but are functions of the local dependent variables. A reiterative matrix solution is required.

The difference equation for B(X,T) is

$$- \gamma_7 B_{i-1,j+1} + \gamma_8 B_{i,j+1} + \gamma_9 B_{i+1,j+1} =$$

$$\gamma_{10} B_{i-1,j} - \gamma_{11} B_{i,j} - \gamma_{12} B_{i+1,j} + \beta_2 \qquad \text{(A-8)}$$

where

$$\gamma_7 = 6kD_b^o + 3hkR_b^o - h^2,$$

$$\gamma_8 = 12kD_b^o + 10h^2 + 3h^2kk_2^o(C_{i,j+1} + C_{i,j}),$$

$$\gamma_9 = 3hkR_b^o - 6kD_b^o + h^2,$$

$$\gamma_{10} = 6kD_b^o + 3hkR_b^o + h^2,$$

$$\gamma_{11} = 12kD_b^o - 10h^2 + 3h^2kk_2(C_{i,j+1} + C_{i,j}),$$

$$\gamma_{12} = 3hkR_b^o - 6kD_b^o - h^2,$$

$$\beta_2 = 3h^2kk_1^o(A_{i,j+1} + A_{i,j})^2.$$

For C(X,T), the difference equation is

$$- \gamma_{13} C_{i-1,j+1} + \gamma_{14} C_{i,j+1} + \gamma_{15} C_{i+1,j+1} =$$

$$\gamma_{16} C_{i-1,j} - \gamma_{17} C_{i,j} - \gamma_{18} C_{i+1,j} + \beta_2 \qquad \text{(A-9)}$$

with

$$\gamma_{13} = 6kD_c^o + 3hkR_c^o - h^2,$$

$$\gamma_{14} = 12kD_c^o + 10h^2 + 3h^2kk_2^o(B_{i,j+1} + B_{i,j}),$$

$$\gamma_{15} = 3hkR_c^o - 6hD_c^o + h^2,$$

$$\gamma_{16} = 6kD_c^o + 3hkR_c^o + h^2,$$

$$\gamma_{17} = 12kD_c^o - 10h^2 + 3h^2kk_2^o(B_{i,j+1} + B_{i,j}),$$

$$\gamma_{18} = 3hkR_c^o - 6kD_c^o - h^2.$$

Again, matrix coefficients γ_8, γ_{11}, γ_{14}, γ_{17}, and β_2 are functions of the local dependent variables requiring reiterative solution techniques.

Substitution of the finite difference equations gives a non-linear tridiagonal matrix for each dependent variable. A simple method for solving tridiagonal matrices was given by Thomas (35). While equivalent to a Gaussian elimination technique, the computational algorithm avoids the error growth in the back solution of the Gaussian elimination. In addition, computer storage requirements are minimized. An outline of the algorithm follows.

For the system of n simultaneous linear equations given by

$$b_1x_1 + c_1x_2 = d_1,$$

$$a_rx_{r-1} + b_rx_r + c_rx_{r+1} = d_r, \qquad r = 2,3,\ldots,n-1,$$

$$a_nx_{n-1} + b_nx_n = d_n,$$

let

$$w_1 = b_1,$$

$$q_{r-1} = \frac{c_{r-1}}{w_{r-1}}, \qquad r = 2,3,\ldots,n,$$

$$w_r = b_r - a_r q_{r-1}, \qquad r = 2,3,\ldots,n$$

and

$$g_1 = \frac{d_1}{w_1},$$

$$g_r = \frac{d_r - a_r g_{r-1}}{w_r}, \qquad r = 2,3,\ldots,n.$$

The solution is given by

$$x_n = g_n,$$

$$x_r = g_r - q_r x_{r+1}, \qquad r = 1,2,\ldots,n-1.$$

The algorithm consists of calculating w, q and g in order of increasing r, followed by the calculation of x in order of decreasing r.

An improvement in the computer application of this algorithm can be made noting that w_r is a local dummy variable which does not require computer storage.

If

$$a_1 = q_o = g_o = c_n = x_{n+1} = 0$$

then for r = 1,2,...,n,

$$w_r = b_r - a_r q_{r-1},$$

$$g_r = \frac{d_r - a_r g_{r-1}}{w_r},$$

$$q_r = \frac{c_r}{w_r},$$

and

$$x_r = g_r - q_r x_{r+1} .$$

This algorithm requires only three multiplications, two divisions, three additions, and two extra storage units for each grid point calculated. The Thomas elimination of a third division by using q_r greatly increases the computer solution speed. The rearrangement of the calculation scheme as outlined requires one-third less algorithm storage than the method given by Thomas, but retains his division savings.

An outline solution of the three finite difference equations (A-7), (A-8), and (A-9) is:

1. Solve the A(X,T) matrix, using previous values of A(X,T), B(X,T), and C(X,T) to calculate the nonlinear matrix coefficients.

2. Solve the B(X,T) matrix, using present values of A(X,T) and the previous values of B(X,T) and C(X,T) to calculate the nonlinear matrix coefficients.

3. Solve the C(X,T) matrix, using present values of A(X,T) and B(X,T) and the previous values of C(X,T) to calculate the nonlinear coefficients.

4. Recalculate steps 1, 2, and 3, using the new values of A(X,T), B(X,T) and C(X,T) until sufficient accuracy between the assumed and calculated values is obtained.

APPENDIX B

COMPUTER PROGRAM FOR NUMERICAL SOLUTION

The calculations were made on a Burroughs B-5500 Information Processing System operated by the Rich Electronic Computer Center at the Georgia Institute of Technology. The program language was Extended Algol 60.

Outline

The computer program has been broken into functional sections preceded by COMMENT SECTION statements. An outline description of each section can be found following the section heading.

SECTION (I). The required program declarations of variables and input-output lists and formats are included in this section. Input-output equipment mode control and program labels are also presented. A procedure is listed allowing interruption of long program calculations every 600 seconds.

SECTION (II). In Section II, input data are read into the program and stored for as many cases as desired. The input data contain an initial square wave concentration profile, diffusion coefficient, and column velocity for each component. Forward and reverse reaction rates, initial and final grid mesh, and variable test errors are specified. The first case to be calculated is retrieved and an output printing made of the input data.

SECTION (III). Initial program constants and the initial square wave concentration profile are set for each component. The matrix coefficients which are constant are evaluated.

SECTION (IV). Detailed control of the numerical calculation program is maintained in this section. At fixed times, concentration profiles of A(X,T), B(X,T), and C(X,T) are printed. As the components spread by diffusion, the grid mesh can be increased without an appreciable truncation error. Therefore, a much faster calculation is possible. This modification is accomplished separately for h and k.

Initially all three components are entirely contained within a small portion of the column near the entrance. At some later time, the front of the column is again empty. It would be wasteful and require extremely long computation times to include the entire column length in every time level calculation. For this reason, the program was designed to allow calculation within the column portion containing all three components. Column sections near the entrance are effectively removed from the calculation scheme once those sections are empty. When the fastest component nears the end of the first section, additional sections are added until the column exit is passed.

The column is continually monitored to determine when all of the components have emerged from the column. At this time, the stored exit concentration of components A, B and C is printed. If there are additional input data sets stored, a new calculation is started; otherwise, the program is stopped.

SECTION (V). The reiterative solutions of the nonlinear matrices

for A(X,T), B(X,T), and C(X,T) are obtained using the outlined technique of Appendix A. After sufficient iterations, the present time values at (t - k) are replaced by the values at t and the calculations started for time (t + k). In addition, the column exit is monitored and the exit concentration stored as a function of time to be later printed under section IV.

Computer Program Nomenclature

DIFFA	- D_a^o	GAMMA17	- γ_{17}
DIFFB	- D_b^o	GAMMA18	- γ_{18}
DIFFC	- D_c^o	H	- h
GAMMA1	- γ_1	K	- k
GAMMA2	- γ_2	K1	- k_1^o
GAMMA3	- γ_3	K2	- k_2^o
GAMMA4	- γ_4	RA	- R_a^o
GAMMA5	- γ_5	RB	- R_b^o
GAMMA6	- γ_6	RC	- R_c^o
GAMMA7	- γ_7	T	- T
GAMMA8	- γ_8	A0[ ]	- $A_{i,j}$
GAMMA9	- γ_9	A1[ ]	- $A_{i,j+1(estimated)}$
GAMMA10	- γ_{10}	A2[ ]	- $A_{i,j+1}$
GAMMA11	- γ_{11}	B0[ ]	- $B_{i,j}$
GAMMA12	- γ_{12}	B1[ ]	- $B_{i,j+1(estimated)}$
GAMMA13	- γ_{13}	B2[ ]	- $B_{i,j+1}$
GAMMA14	- γ_{14}	C0[ ]	- $C_{i,j}$
GAMMA15	- γ_{15}	C1[ ]	- $C_{i,j+1(estimated)}$
GAMMA16	- γ_{16}	C2[ ]	- $C_{i,j+1}$

```
BEGIN COMMENT INCREASED EQUILIBRIUM YIELDS OF REACTION 2A = B + C  USING
              GAS CHROMATOGRAPHIC SEPARATION AND STUDYING THE EFFECTS OF
              KINETICS AND DIFFUSION ;

COMMENT SECTION(I), PROGRAM DECLARATIONS ;
INTEGER I,J,L,M,N,P,Q,R,R1,R2,R3,S,CYCLES,FLAG1,DISPLACEMENT ;
INTEGER ARRAY DUM1[0:2,0:10] ;
REAL  GAMMA1,GAMMA2,GAMMA3,GAMMA4,GAMMA5,GAMMA6,GAMMA7,GAMMA8,GAMMA9,
      GAMMA10,GAMMA11,GAMMA12,GAMMA13,GAMMA14,GAMMA15,GAMMA16,GAMMA17,
      GAMMA18,CON1,CON2,CON3,CON4,CON5,CON6,CON7,CON8,CON9,CON10,H,K,
      HMAX,KMAX,DIFFA,DIFFB,DIFFC,RA,RB,RC,K1,K2,ERROR1,ERROR2,A0,B0,C0,
      T,T0,T1,T2,T3,MOLEA,MOLEB,MOLEC,MOLED,MOLEE,W,E ;
ARRAY A0,A1,A2,B0,B1,B2,C0,C1,C2,ALPH,G[0:500],DUM2[0:17,0:10],
       A3,B3,C3,DUM3[0:200] ;
FORMAT FMT0 (I2) ;
FORMAT FMT1 (2I3,X10,4F16.10/(5F16.10)) ;
LIST LST1 (DUM1[1,I],DUM1[2,I], FOR J = 1 STEP 1 UNTIL 17 DO
           DUM2[J,I] ) ;
FORMAT FMT2 (////////////X29,"CHROMATOGRAPHIC REACTOR INPUT DATA",
```

```
" = INFINITE COLUMN"///X25,
"COLUMN DISPLACEMENT = L = ",I3," SPACE UNITS"//X25,
"STEP FUNCTION WIDTH = M = ",I3," SPACE UNITS"//X25,
"INITIAL SPACE DIFFERENCE UNIT = H = ",F16.10//X25,
"INITIAL TIME  DIFFERENCE UNIT = K = ",F16.10//X25,
"FINAL   SPACE DIFFERENCE UNIT = HMAX  = ",F16.10//X25,
"FINAL   TIME  DIFFERENCE UNIT = KMAX  = ",F16.10//X25,
"DIFFUSION COEFFICIENT, COMPONENT A = DIFFA =",F16.10//X25,
"DIFFUSION COEFFICIENT, COMPONENT B = DIFFB =",F16.10//X25,
"DIFFUSION COEFFICIENT, COMPONENT C = DIFFC =",F16.10//X25,
"COLUMN VELOCITY, COMPONENT A = RA = ",F16.10//X25,
"COLUMN VELOCITY, COMPONENT B = RB = ",F16.10//X25,
"COLUMN VELOCITY, COMPONENT C = RC = ",F16.10//X25,
"FORWARD REACTION RATE = K1 = ",F16.10//X25,
"REVERSE REACTION RATE = K2 = ",F16.10//X25,
"REITERATION COMPLETENESS TEST ERROR = ERROR1 = ",F16.10//
X25,"COMPONENT PEAK PROGRESS  TEST ERROR = ERROR2 = ",
F16.10//
X25,"INITIAL CONCENTRATION, COMPONENT A = A0 = ",F16.10//
```

```
              X25,"INITIAL CONCENTRATION, COMPONENT B = BO = ",F16.10//
              X25,"INITIAL CONCENTRATION, COMPONENT C = CO = ",F16.10) ;
LIST LST2  ( L,M,H,K,MMAX,KMAX,DIFFA,DIFFB,DIFFC,RA,RB,RC,K1,K2,ERROR1,
              ERROR2,AO,BO,CO) ;
FORMAT FMT3 (X18,"CYCLES = ",I3, X4,"PROCESS TIME = ",F7.2," SECONDS",
              X4, "INPUT-OUTPUT TIME = ",F7.2," SECONDS"//X18,"T = ",
              F10.8,X10,"J = ",I4,X14,"H = ",F10.8,X10,"K = ",F10.8,///
              X20,"I",X3,"A(I,T)",X3,"B(I,T)",X3,"C(I,T)",X3,"SUM(I)",
              X9,"I",X3,"A(I,T)", X3,"B(I,T)",X3,"C(I,T)",X3,"SUM(I)",
              X17//50(X18,I3,4(X1,F8.4),X7,I3,4(X1,F8.4)/) //X18,
              "DISPLACEMENT = ",I4,X17,"MOLE FRACTION",4(X1,F8.4)) ;
LIST LST3 (CYCLES,T2,T3,T,J,H,K,FOR I ← R STEP R UNTIL R2 DO
             [I, AO[I], BO[I], CO[I],  G[I]],DISPLACEMENT,MOLEA,MOLEB,
             MOLEC,MOLED) ;
FORMAT FMT4 (/X27,"2A = B + C  CHROMATOGRAPH EXIT CONCENTRATION AS A ",
              "FUNCTION OF TIME",////X19,"TIME",X2,"A(1,T)",X2,
              "B(1,T)",X2,"C(1,T)",X2,"SUM(T)",X12,"TIME",X2,"A(1,T)",
              X2,"B(1,T)",X2,"C(1,T)",X2,"SUM(T)"//(X18,F5.3,4(X1,
              F7.4),X11,F5.3,4(X1,F7.4),X17)) ;
```

```
LIST LST4 ( FOR I ← 1 STEP 1 UNTIL  Q  DO [DUM3[I], A3[I], B3[I], C3[I],
                G[I]]) ;
FORMAT FMT5 (//X53,"EXIT MOLE FRACTION",4(X1,F7.4)) ;
LIST LST5 (MOLEA,MOLEB,MOLEC,MOLED ) ;
FILE IN CARD (2,10) ;
FILE OUT PRINT 6(2,15) ;
LABEL L1,L2,L3,L4,L5,L6,L7 ;
 INTEGER X789;          PROCEDURE BRKTIME; IF TIME(2) ≥ X789 THEN BEGIN
 X789 := X789 + 36000 ; BREAK   END ;  X789 := 36000 ;

COMMENT SECTION(II), DATA INPUT, STORAGE, RETRIVAL AND PRINTING ;
COMMENT DATA INPUT AND STORAGE ;
               READ ( CARD,FMT0,N ) ;
          FOR I ← 1 STEP 1 UNTIL N DO
               READ ( CARD,FMT1,LST1 ) ;
               CLOSE ( CARD,RELEASE ) ;
               P ← 0 ;
L3: COMMENT INPUT DATA RETRIVAL ;
               P ← P + 1 ;
```

```
L ← DUM1[1,P] ;
M ← DUM1[2,P] ;
H ← DUM2[1,P] ;
K ← DUM2[2,P] ;
HMAX  ← DUM2[3,P] ;
KMAX  ← DUM2[4,P] ;
DIFFA ← DUM2[5,P] ;
DIFFB ← DUM2[6,P] ;
DIFFC ← DUM2[7,P] ;
RA ← DUM2[8,P] ;
RB ← DUM2[9,P] ;
RC ← DUM2[10,P] ;
K1 ← DUM2[11,P] ;
K2 ← DUM2[12,P] ;
ERROR1 ← DUM2[13,P] ;
ERROR2 ← DUM2[14,P] ;
AO ← DUM2[15,P] ;
BO ← DUM2[16,P] ;
CO ← DUM2[17,P] ;
```

```
COMMENT PRINT INPUT DATA ;
        WRITE (PRINT,FMT2,LST2) ;
        WRITE (PRINT [PAGE] ) ;

COMMENT SECTION(III), SET INITIAL CONSTANTS AND INITIAL CONDITIONS,
                      CALCULATE MATRIX CONSTANTS ;
COMMENT SETTING INITIAL CONSTANTS ;
        TO ← TIME(2) ;
        T3 ← J ← CYCLES ← T ← ALPH[0] ← G[0] ← Q ← 0 ;
        DISPLACEMENT ← ENTIER (L + (M/2) + 0,50 ) ;
        MDLEE ← 100×M×H×(A0 + B0 + C0) ;
        R ← FLAG1 ← 1 ;
        R1 ← 100×R - 1 ;
        R2 ← 100×R ;
        R3 ← ENTIER((1/HMAX) + 0,005) + DISPLACEMENT ;
COMMENT SETTING INITIAL CONDITIONS ;
    FOR I ← 0 STEP 1 UNTIL L DO
        A0[I] ← A1[I] ← B0[I] ← B1[I] ← C0[I] ← C1[I] ← 0 ;
    FOR I ← L+1 STEP 1 UNTIL L+M DO
```

```
    BEGIN
              A0[I] ← A1[I] ← A0 ;
              B0[I] ← B1[I] ← B0 ;
              C0[I] ← C1[I] ← C0 ;
    END ;
         FOR I ← L+M+1 STEP 1 UNTIL 500 DO
              A0[I] ← A1[I] ← A2[I] ← B0[I] ← B1[I] ← B2[I] ←
              C0[I] ← C1[I] ← C2[I] ← 0 ;
L5: COMMENT CALCULATION OF CONSTANTS ;
              GAMMA1 ← 6×K×DIFFA + 3×H×K×RA - H×H ;
              GAMMA3 ← 3×H×K×RA - 6×K×DIFFA + H×H ;
              GAMMA4 ← 6×K×DIFFA + 3×H×K×RA + H×H ;
              GAMMA6 ← 3×H×K×RA - 6×K×DIFFA - H×H ;
              GAMMA7 ← 6×K×DIFFB + 3×H×K×RB - H×H ;
              GAMMA9 ← 3×H×K×RB - 6×K×DIFFB + H×H ;
              GAMMA10 ← 6×K×DIFFB + 3×H×K×RB + H×H ;
              GAMMA12 ← 3×H×K×RB - 6×K×DIFFB - H×H ;
              GAMMA13 ← 6×K×DIFFC + 3×H×K×RC - H×H ;
              GAMMA15 ← 3×H×K×RC - 6×K×DIFFC + H×H ;
```

```
            GAMMA16 ← 6×K×DIFFC + 3×H×K×RC + H×H ;
            GAMMA18 ← 3×H×K×RC - 6×K×DIFFC - H×H ;
            CON1 ← 12×K×DIFFA + 10×H×H ;
            CON2 ← 12×K×DIFFA - 10×H×H ;
            CON3 ←  3×H×H×K×K1 ;
            CON4 ←  3×H×H×K×K2 ;
            CON5 ← 12×K×DIFFB + 10×H×H ;
            CON6 ← 12×K×DIFFB - 10×H×H ;
            CON7 ← 12×K×DIFFC + 10×H×H ;
            CON8 ← 12×K×DIFFC - 10×H×H ;
            CON9 ← 6×H×H×K×K1 ;
            CON10 ← 6×H×H×K×K2 ;

COMMENT SECTION (IV), PRINT A, B, C AND MONITOR COMPONENT PROGRESS ;
L2: COMMENT PRINT A(X,T), B(X,T) AND C(X,T) ;
        IF ABS(10×T - 1) < 0.00001 OR
        ABS(5×T - ENTIER(5×T + 0.0001)) < 0.00001 THEN
    BEGIN
            MOLEA ← MOLEB ← MOLEC ← 0 ;
```

```
        FOR I ← 1 STEP 1 UNTIL R2 DO
    BEGIN
              MOLEA ← Ao[I] + MOLEA ;
              MOLEB ← Bo[I] + MOLEB ;
              MOLEC ← Co[I] + MOLEC ;
              G[I]  ←  AO[I] +  Bo[I] +  Co[I] ;
    END ;
              MOLEA ← (100×H×MOLEA)/MOLEE ;
              MOLEB ← (100×H×MOLEB)/MOLEE ;
              MOLEC ← (100×H×MOLEC)/MOLEE ;
              MOLED ← MOLEA + MOLEB + MOLEC ;
              T2 ← (TIME(2) - T0)/60 ;
              T1 ← TIME(3) ;
              WRITE (PRINT,FMT3,LST3) ;
              WRITE (PRINT [PAGE] ) ;
              T3 ← T3 + (TIME(3) - T1)/60 ;
    END ;
 BRKTIME ;
COMMENT COMPONENT PROGRESS TESTS ;
```

```
COMMENT INCREASE TIME DIFFERENCE UNIT, K ;
        IF (KMAX - K) > 0,00001 THEN
        IF FLAG1 = 1 AND (J = 80 OR J = 140 OR J = 180 OR J = 220 OR
           J = 280 OR J = 320 OR J = 360 OR J = 420 OR J = 460) THEN
    BEGIN
            K ← T/40 ;
            FLAG1 ← 0 ;
            GO TO L5 ;
    END ;
COMMENT INCREASE SPACE DIFFERENCE UNIT, H AND RESET MATRICES ;
        IF (HMAX - H) > 0,00001 THEN
        IF (  A0[99] ≥ ERROR2 OR  B0[99] ≥ ERROR2 OR  C0[99] ≥ ERROR2 )
        THEN
    BEGIN
            S ← ENTIER ((0,005/H) + 0,50) ;
            DISPLACEMENT ← ENTIER ((DISPLACEMENT/2) + S + 0,50 ) ;
            R3 ← ENTIER((1/HMAX) + 0,005) + DISPLACEMENT ;
            H ← 2×H ;
        FOR I ← 1 STEP 1 UNTIL 49 DO
```

```
    BEGIN
              A0[I+S]  ←  A1[I+S] ←  A2[2×I] ;
              B0[I+S]  ←  B1[I+S] ←  B2[2×I] ;
              C0[I+S]  ←  C1[I+S] ←  C2[2×I] ;
    END ;
         FOR I ← 1 STEP 1 UNTIL S DO
              A0[I]  ←  A1[I] ←  B0[I] ←  B1[I] ←  C0[I] ←  C1[I] ← 0 ;
         FOR I ← ( 50 + S ) STEP 1 UNTIL 100 DO
              A0[I]  ←  A1[I] ←  B0[I] ←  B1[I] ←  C0[I] ←  C1[I] ← 0 ;
              FLAG1 ← 0 ;
              GO TO L5 ;
    END
         ELSE GO TO L6 ;
COMMENT DISPLACE SOLUTION TOWARD ORIGIN ;
         FOR I ← 40 STEP -1 UNTIL 1 DO
         IF A0[I] ≥ ERROR2 OR B0[I] ≥ ERROR2 OR C0[I] ≥ ERROR2 THEN
              GO TO L7 ;
         FOR I ← 1 STEP 1 UNTIL (R1 - 25) DO
    BEGIN
```

```
            A0[I] ← A1[I] ← A2[ I + 25] ;
            B0[I] ← B1[I] ← B2[ I + 25] ;
            C0[I] ← C1[I] ← C2[ I + 25] ;
    END ;
        FOR I ← (R1 - 24) STEP 1 UNTIL R1 DO
            A0[I] ← A1[I] ← B0[I] ← B1[I] ← C0[I] ← C1[I] ← 0 ;
            DISPLACEMENT ← DISPLACEMENT - 25 ;
            R3 ← ENTIER((1/HMAX) + 0,005) + DISPLACEMENT ;
L7: COMMENT MODIFY   COLUMN SOLUTION LENGTH ;
        IF R3 > (R1 - 50) THEN
        IF ( A0[R1] ≥ ERROR2 OR B0[R1] ≥ ERROR2 OR C0[R1] ≥ ERROR2 )
        THEN
    BEGIN
            R ← R + 1 ;
            R1 ← 100×R - 1 ;
            R2 ← 100×R ;
    END ;
        IF R3 ≥ R1 THEN GO TO L6 ;
        IF R3 < (R1 - 150) THEN
```

```
    BEGIN
              R ← R - 1 ;
              R1 ← 100×R - 1 ;
              R2 ← 100×R ;
              A0[R2] ← A1[R2] ← A2[R2] ← B0[R2] ← B1[R2] ← B2[R2] ←
              C0[R2] ← C1[R2] ← C2[R2] ← 0 ;
    END ;
COMMENT CHECK IF COLUMN IS EMPTY ;
         FOR I ← R3  STEP -1 UNTIL 1 DO
         IF  A0[I] ≥ ERROR2 OR  B0[I] ≥ ERROR2 OR  C0[I] ≥ ERROR2 THEN
              GO TO L6 ;
COMMENT WHEN COLUMN IS EMPTY, PRINT EXIT CONCENTRATION CHROMATOGRAPH ;
              MOLEA ← MOLEB ← MOLEC ← 0 ;
         FOR I ← 1 STEP 1 UNTIL 9 DO
    BEGIN
              MOLEA ← A3[I] + MOLEA ;
              MOLEB ← B3[I] + MOLEB ;
              MOLEC ← C3[I] + MOLEC ;
              G[I]  ←   A3[I] +  B3[I] +  C3[I] ;
```

```
    END ;
                MOLEA ← (RA×MOLEA)/MOLEE ;
                MOLEB ← (RB×MOLEB)/MOLEE ;
                MOLEC ← (RC×MOLEC)/MOLEE ;
                MOLED ← MOLEA + MOLEB + MOLEC ;
                WRITE ( PRINT,FMT4,LST4) ;
                WRITE ( PRINT,FMT5,LST5) ;
                WRITE ( PRINT [PAGE] ) ;
COMMENT INPUT DATA STORAGE CHECK ;
          IF P < N THEN
                GO TO L3
          ELSE GO TO L4 ;

COMMENT SECTION (V), CALCULATE A(X,T), B(X,T) AND C(X,T) ;
L6:             FLAG1 ← 1 ;
                J ← J + 1 ;
                T ← T + K ;
                CYCLES ← 1 ;
L1:  COMMENT CALCULATION OF A(X,T) ;
```

```
        FOR I ← 1 STEP 1 UNTIL R1 DO
    BEGIN
            GAMMA2 ← CON9×(A0[I] + A1[I]) + CON1 ;
            GAMMA5 ← CON9×(A0[I] + A1[I]) + CON2 ;
            E ← CON10×(B0[I] + B1[I])×(C0[I] + C1[I]) +
            GAMMA4×A0[I-1] - GAMMA5×A0[I] - GAMMA6×A0[I+1] ;
            W ← GAMMA1×ALPH[I-1] + GAMMA2 ;
            G[I] ← (GAMMA1×G[I-1] + E)/W ;
            ALPH[I] ← GAMMA3/W ;
    END ;
        FOR I ← R1 STEP -1 UNTIL 1 DO
            A2[I]  ← G[I] - ALPH[I]×A2[I+1] ;
COMMENT CALCULATION OF B(X,T) ;
        FOR I ← 1 STEP 1 UNTIL R1 DO
    BEGIN
            GAMMA8 ← CON4×(C0[I] + C1[I]) + CON5 ;
            GAMMA11 ← CON4×(C0[I] + C1[I]) + CON6 ;
            E ← CON3×(A0[I] + A2[I])×(A0[I] + A2[I]) +
            GAMMA10×B0[I-1] - GAMMA11×B0[I] - GAMMA12×B0[I+1] ;
```

```
            W ← GAMMA7×ALPH[I-1] + GAMMA8 ;
            G[I] ← (GAMMA7×G[I-1] + E)/W ;
            ALPH[I] ← GAMMA9/W ;
    END ;
        FOR I ← R1 STEP -1 UNTIL 1 DO
            B2[I]  ← G[I] - ALPH[I]×B2[I+1] ;
COMMENT CALCULATION OF C(X,T) ;
        FOR I ← 1 STEP 1 UNTIL R1 DO
    BEGIN
            GAMMA14 ← CON4×(B0[I] + B2[I]) + CON7 ;
            GAMMA17 ← CON4×(B0[I] + B2[I]) + CON8 ;
            E ← CON3×(A0[I] + A2[I])×(A0[I] + A2[I]) +
            GAMMA16×C0[I-1] - GAMMA17×C0[I] - GAMMA18×C0[I+1] ;
            W ← GAMMA13×ALPH[I-1] + GAMMA14 ;
            G[I] ← (GAMMA13×G[I-1] + E)/W ;
            ALPH[I] ← GAMMA15/W ;
    END ;
        FOR I ← R1 STEP -1 UNTIL 1 DO
            C2[I]  ← G[I] - ALPH[I]×C2[I+1] ;
```

```
COMMENT REITERATION COMPLETENESS TEST ;
        IF K1 ≠ 0.0 OR  K2 ≠ 0.0 THEN
        FOR I ← 1 STEP 1 UNTIL R1 DO
        IF ABS( A2[I] -  A1[I]) ≥ ERROR1 OR
           ABS( B2[I] -  B1[I]) ≥ ERROR1 OR
           ABS( C2[I] -  C1[I]) ≥ ERROR1 THEN
    BEGIN
COMMENT REPLACE FIRST APPROXIAMATIONS BY CALCULATED VALUES ;
        FOR I ← 1 STEP 1 UNTIL R1 DO
    BEGIN
            A1[I]  ←  A2[I] ;
            B1[I]  ←  B2[I] ;
            C1[I]  ←  C2[I] ;
    END ;
            CYCLES ← CYCLES + 1 ;
            GO TO L1 ;
    END ;
COMMENT REPLACE PRESENT BOUNDARY VALUES BY CALCULATED VALUES FOR NEXT
        CALCULATION ;
```

```
        FOR I ← 1 STEP 1 UNTIL R1 DO
    BEGIN
            A0[I]  ←  A1[I] ←  A2[I] ;
            B0[I]  ←  B1[I] ←  B2[I] ;
            C0[I]  ←  C1[I] ←  C2[I] ;
    END ;
        IF R3 ≥ R1 THEN GO TO L2 ;
COMMENT STORE EXIT CONCENTRATION AS A FUNCTION OF TIME ;
        IF ABS(100×T - ENTIER(100×T + 0.0001)) < 0.0001 THEN
        IF M = 0 OR (A0[R3] ≥ ERROR2 OR B0[R3] ≥ ERROR2 OR
           C0[R3] ≥ ERROR2) THEN
    BEGIN
            Q ← Q + 1 ;
            A3[Q]  ←  A0[R3] ;
            B3[Q]  ←  B0[R3] ;
            C3[Q]  ←  C0[R3] ;
            DUM3[Q] ← T ;
            M ← 0 ;
    END ;
```

```
                    GO TO L2 ;
L4: END.
```

CHROMATOGRAPHIC REACTOR INPUT DATA - INFINITE COLUMN

COLUMN DISPLACEMENT = L = 54 SPACE UNITS
STEP FUNCTION WIDTH = M = 20 SPACE UNITS

INITIAL SPACE DIFFERENCE UNIT = H = 0.0001562500
INITIAL TIME DIFFERENCE UNIT = K = 0.0000100000

FINAL SPACE DIFFERENCE UNIT = HMAX = 0.0050000000
FINAL TIME DIFFERENCE UNIT = KMAX = 0.0050000000

DIFFUSION COEFFICIENT, COMPONENT A = DIFFA = 0.0020000000
DIFFUSION COEFFICIENT, COMPONENT B = DIFFB = 0.0020000000
DIFFUSION COEFFICIENT, COMPONENT C = DIFFC = 0.0020000000

COLUMN VELOCITY, COMPONENT A = RA = 1.0000000000
COLUMN VELOCITY, COMPONENT B = RB = 0.8000000000
COLUMN VELOCITY, COMPONENT C = RC = 1.3333333330

FORWARD REACTION RATE = K1 = 20.0000000000
REVERSE REACTION RATE = K2 = 40.0000000000

REITERATION COMPLETENESS TEST ERROR = ERROR1 = 0.0000500000
COMPONENT PEAK PROGRESS TEST ERROR = ERROR2 = 0.0000100000

INITIAL CONCENTRATION, COMPONENT A = A0 = 4.1421356200
INITIAL CONCENTRATION, COMPONENT B = B0 = 2.9289321900
INITIAL CONCENTRATION, COMPONENT C = C0 = 2.9289321900

2A = B + C COLUMN CONCENTRATION AS A FUNCTION OF DISTANCE

CYCLES = 0 PROCESS TIME = 0.37 SECONDS INPUT-OUTPUT TIME = 0.00 SECONDS
T = 0.00000000 J = 0 H = 0.00015625 K = 0.00001000

I	A(I,T)	B(I,T)	C(I,T)	SUM(I)	I	A(I,T)	B(I,T)	C(I,T)	SUM(I)
1	0.0000	0.0000	0.0000	0.0000	2	0.0000	0.0000	0.0000	0.0000
3	0.0000	0.0000	0.0000	0.0000	4	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	6	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	8	0.0000	0.0000	0.0000	0.0000
9	0.0000	0.0000	0.0000	0.0000	10	0.0000	0.0000	0.0000	0.0000
11	0.0000	0.0000	0.0000	0.0000	12	0.0000	0.0000	0.0000	0.0000
13	0.0000	0.0000	0.0000	0.0000	14	0.0000	0.0000	0.0000	0.0000
15	0.0000	0.0000	0.0000	0.0000	16	0.0000	0.0000	0.0000	0.0000
17	0.0000	0.0000	0.0000	0.0000	18	0.0000	0.0000	0.0000	0.0000
19	0.0000	0.0000	0.0000	0.0000	20	0.0000	0.0000	0.0000	0.0000
21	0.0000	0.0000	0.0000	0.0000	22	0.0000	0.0000	0.0000	0.0000
23	0.0000	0.0000	0.0000	0.0000	24	0.0000	0.0000	0.0000	0.0000
25	0.0000	0.0000	0.0000	0.0000	26	0.0000	0.0000	0.0000	0.0000
27	0.0000	0.0000	0.0000	0.0000	28	0.0000	0.0000	0.0000	0.0000
29	0.0000	0.0000	0.0000	0.0000	30	0.0000	0.0000	0.0000	0.0000
31	0.0000	0.0000	0.0000	0.0000	32	0.0000	0.0000	0.0000	0.0000
33	0.0000	0.0000	0.0000	0.0000	34	0.0000	0.0000	0.0000	0.0000
35	0.0000	0.0000	0.0000	0.0000	36	0.0000	0.0000	0.0000	0.0000
37	0.0000	0.0000	0.0000	0.0000	38	0.0000	0.0000	0.0000	0.0000
39	0.0000	0.0000	0.0000	0.0000	40	0.0000	0.0000	0.0000	0.0000
41	0.0000	0.0000	0.0000	0.0000	42	0.0000	0.0000	0.0000	0.0000
43	0.0000	0.0000	0.0000	0.0000	44	0.0000	0.0000	0.0000	0.0000
45	0.0000	0.0000	0.0000	0.0000	46	0.0000	0.0000	0.0000	0.0000
47	0.0000	0.0000	0.0000	0.0000	48	0.0000	0.0000	0.0000	0.0000
49	0.0000	0.0000	0.0000	0.0000	50	0.0000	0.0000	0.0000	0.0000

COLUMN CONCENTRATION AS A FUNCTION OF DISTANCE (CONTINUED)

I	A(I,T)	B(I,T)	C(I,T)	SUM(I)	I	A(I,T)	B(I,T)	C(I,T)	SUM(I)
51	0.0000	0.0000	0.0000	0.0000	52	0.0000	0.0000	0.0000	0.0000
53	0.0000	0.0000	0.0000	0.0000	54	0.0000	0.0000	0.0000	0.0000
55	4.1421	2.9289	2.9289	10.0000	56	4.1421	2.9289	2.9289	10.0000
57	4.1421	2.9289	2.9289	10.0000	58	4.1421	2.9289	2.9289	10.0000
59	4.1421	2.9289	2.9289	10.0000	60	4.1421	2.9289	2.9289	10.0000
61	4.1421	2.9289	2.9289	10.0000	62	4.1421	2.9289	2.9289	10.0000
63	4.1421	2.9289	2.9289	10.0000	64	4.1421	2.9289	2.9289	10.0000
65	4.1421	2.9289	2.9289	10.0000	66	4.1421	2.9289	2.9289	10.0000
67	4.1421	2.9289	2.9289	10.0000	68	4.1421	2.9289	2.9289	10.0000
69	4.1421	2.9289	2.9289	10.0000	70	4.1421	2.9289	2.9289	10.0000
71	4.1421	2.9289	2.9289	10.0000	72	4.1421	2.9289	2.9289	10.0000
73	4.1421	2.9289	2.9289	10.0000	74	4.1421	2.9289	2.9289	10.0000
75	0.0000	0.0000	0.0000	0.0000	76	0.0000	0.0000	0.0000	0.0000
77	0.0000	0.0000	0.0000	0.0000	78	0.0000	0.0000	0.0000	0.0000
79	0.0000	0.0000	0.0000	0.0000	80	0.0000	0.0000	0.0000	0.0000
81	0.0000	0.0000	0.0000	0.0000	82	0.0000	0.0000	0.0000	0.0000
83	0.0000	0.0000	0.0000	0.0000	84	0.0000	0.0000	0.0000	0.0000
85	0.0000	0.0000	0.0000	0.0000	86	0.0000	0.0000	0.0000	0.0000
87	0.0000	0.0000	0.0000	0.0000	88	0.0000	0.0000	0.0000	0.0000
89	0.0000	0.0000	0.0000	0.0000	90	0.0000	0.0000	0.0000	0.0000
91	0.0000	0.0000	0.0000	0.0000	92	0.0000	0.0000	0.0000	0.0000
93	0.0000	0.0000	0.0000	0.0000	94	0.0000	0.0000	0.0000	0.0000
95	0.0000	0.0000	0.0000	0.0000	96	0.0000	0.0000	0.0000	0.0000
97	0.0000	0.0000	0.0000	0.0000	98	0.0000	0.0000	0.0000	0.0000
99	0.0000	0.0000	0.0000	0.0000	100	0.0000	0.0000	0.0000	0.0000
DISPLACEMENT = 64					MOLE FRACTION	0.4142	0.2929	0.2929	1.0000

2A = B + C COLUMN CONCENTRATION AS A FUNCTION OF DISTANCE

CYCLES = 2 PROCESS TIME = 31.07 SECONDS INPUT-OUTPUT TIME = 0.72 SECONDS
T = 0.40000000 J = 460 H = 0.00500000 K = 0.00500000

I	A(I,T)	B(I,T)	C(I,T)	SUM(I)	I	A(I,T)	B(I,T)	C(I,T)	SUM(I)
2	0.0000	0.0000	0.0000	0.0000	4	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	8	0.0000	0.0000	0.0000	0.0000
10	0.0000	0.0000	0.0000	0.0000	12	0.0000	0.0000	0.0000	0.0000
14	0.0000	0.0000	0.0000	0.0000	16	0.0000	0.0000	0.0000	0.0000
18	0.0000	0.0000	0.0000	0.0000	20	0.0000	0.0000	0.0000	0.0000
22	0.0000	0.0001	0.0000	0.0001	24	0.0000	0.0002	0.0000	0.0002
26	0.0000	0.0006	0.0000	0.0006	28	0.0000	0.0013	0.0000	0.0013
30	0.0000	0.0028	0.0000	0.0028	32	0.0000	0.0055	0.0000	0.0055
34	0.0000	0.0101	0.0000	0.0101	36	0.0000	0.0173	0.0000	0.0174
38	0.0001	0.0277	0.0000	0.0278	40	0.0002	0.0413	0.0000	0.0415
42	0.0004	0.0577	0.0000	0.0581	44	0.0010	0.0754	0.0000	0.0764
46	0.0021	0.0925	0.0000	0.0946	48	0.0041	0.1066	0.0000	0.1106
50	0.0071	0.1156	0.0000	0.1228	52	0.0115	0.1185	0.0001	0.1301
54	0.0173	0.1148	0.0002	0.1323	56	0.0241	0.1055	0.0005	0.1301
58	0.0314	0.0923	0.0010	0.1247	60	0.0385	0.0770	0.0018	0.1173
62	0.0447	0.0614	0.0030	0.1091	64	0.0492	0.0469	0.0047	0.1008
66	0.0517	0.0343	0.0068	0.0928	68	0.0519	0.0241	0.0094	0.0854
70	0.0499	0.0161	0.0125	0.0785	72	0.0457	0.0103	0.0164	0.0724
74	0.0400	0.0062	0.0213	0.0675	76	0.0333	0.0035	0.0277	0.0645
78	0.0263	0.0018	0.0361	0.0642	80	0.0197	0.0009	0.0469	0.0675
82	0.0139	0.0004	0.0600	0.0742	84	0.0093	0.0002	0.0744	0.0838
86	0.0058	0.0001	0.0886	0.0945	88	0.0035	0.0000	0.1007	0.1042
90	0.0020	0.0000	0.1086	0.1105	92	0.0011	0.0000	0.1109	0.1120
94	0.0005	0.0000	0.1073	0.1078	96	0.0003	0.0000	0.0982	0.0985
98	0.0001	0.0000	0.0853	0.0854	100	0.0001	0.0000	0.0703	0.0703

COLUMN CONCENTRATION AS A FUNCTION OF DISTANCE (CONTINUED)

I	A(I,T)	B(I,T)	C(I,T)	SUM(I)	I	A(I,T)	B(I,T)	C(I,T)	SUM(I)
102	0.0000	0.0000	0.0550	0.0551	104	0.0000	0.0000	0.0410	0.0410
106	0.0000	0.0000	0.0291	0.0292	108	0.0000	0.0000	0.0198	0.0198
110	0.0000	0.0000	0.0128	0.0128	112	0.0000	0.0000	0.0080	0.0080
114	0.0000	0.0000	0.0048	0.0048	116	0.0000	0.0000	0.0027	0.0027
118	0.0000	0.0000	0.0015	0.0015	120	0.0000	0.0000	0.0008	0.0008
122	0.0000	0.0000	0.0004	0.0004	124	0.0000	0.0000	0.0002	0.0002
126	0.0000	0.0000	0.0001	0.0001	128	0.0000	0.0000	0.0000	0.0000
130	0.0000	0.0000	0.0000	0.0000	132	0.0000	0.0000	0.0000	0.0000
134	0.0000	0.0000	0.0000	0.0000	136	0.0000	0.0000	0.0000	0.0000
138	0.0000	0.0000	0.0000	0.0000	140	0.0000	0.0000	0.0000	0.0000
142	0.0000	0.0000	0.0000	0.0000	144	0.0000	0.0000	0.0000	0.0000
146	0.0000	0.0000	0.0000	0.0000	148	0.0000	0.0000	0.0000	0.0000
150	0.0000	0.0000	0.0000	0.0000	152	0.0000	0.0000	0.0000	0.0000
154	0.0000	0.0000	0.0000	0.0000	156	0.0000	0.0000	0.0000	0.0000
158	0.0000	0.0000	0.0000	0.0000	160	0.0000	0.0000	0.0000	0.0000
162	0.0000	0.0000	0.0000	0.0000	164	0.0000	0.0000	0.0000	0.0000
166	0.0000	0.0000	0.0000	0.0000	168	0.0000	0.0000	0.0000	0.0000
170	0.0000	0.0000	0.0000	0.0000	172	0.0000	0.0000	0.0000	0.0000
174	0.0000	0.0000	0.0000	0.0000	176	0.0000	0.0000	0.0000	0.0000
178	0.0000	0.0000	0.0000	0.0000	180	0.0000	0.0000	0.0000	0.0000
182	0.0000	0.0000	0.0000	0.0000	184	0.0000	0.0000	0.0000	0.0000
186	0.0000	0.0000	0.0000	0.0000	188	0.0000	0.0000	0.0000	0.0000
190	0.0000	0.0000	0.0000	0.0000	192	0.0000	0.0000	0.0000	0.0000
194	0.0000	0.0000	0.0000	0.0000	196	0.0000	0.0000	0.0000	0.0000
198	0.0000	0.0000	0.0000	0.0000	200	0.0000	0.0000	0.0000	0.0000
DISPLACEMENT = -13					MOLE FRACTION	0.1878	0.4061	0.4061	1.0000

2A = B + C CHROMATOGRAPH EXIT CONCENTRATION AS A FUNCTION OF TIME

TIME	A(1,T)	B(1,T)	C(1,T)	SUM(T)	TIME	A(1,T)	B(1,T)	C(1,T)	SUM(T)
0.600	0.0000	0.0000	0.0001	0.0001	0.620	0.0000	0.0000	0.0004	0.0004
0.640	0.0000	0.0000	0.0017	0.0017	0.660	0.0000	0.0000	0.0058	0.0058
0.680	0.0000	0.0000	0.0156	0.0156	0.700	0.0000	0.0000	0.0333	0.0333
0.720	0.0000	0.0000	0.0566	0.0566	0.740	0.0000	0.0000	0.0768	0.0768
0.760	0.0000	0.0000	0.0841	0.0841	0.780	0.0001	0.0000	0.0752	0.0753
0.800	0.0002	0.0000	0.0563	0.0565	0.820	0.0005	0.0000	0.0369	0.0374
0.840	0.0013	0.0000	0.0227	0.0240	0.860	0.0028	0.0000	0.0143	0.0171
0.880	0.0051	0.0001	0.0098	0.0150	0.900	0.0083	0.0002	0.0073	0.0158
0.920	0.0119	0.0005	0.0057	0.0181	0.940	0.0153	0.0011	0.0045	0.0209
0.960	0.0179	0.0020	0.0035	0.0234	0.980	0.0194	0.0033	0.0026	0.0253
1.000	0.0197	0.0050	0.0019	0.0265	1.020	0.0187	0.0073	0.0012	0.0271
1.040	0.0166	0.0102	0.0007	0.0276	1.060	0.0138	0.0141	0.0004	0.0284
1.080	0.0108	0.0192	0.0002	0.0301	1.100	0.0077	0.0256	0.0001	0.0334
1.120	0.0051	0.0334	0.0000	0.0385	1.140	0.0031	0.0421	0.0000	0.0452
1.160	0.0017	0.0511	0.0000	0.0529	1.180	0.0009	0.0596	0.0000	0.0605
1.200	0.0004	0.0664	0.0000	0.0668	1.220	0.0002	0.0707	0.0000	0.0709
1.240	0.0001	0.0718	0.0000	0.0719	1.260	0.0000	0.0696	0.0000	0.0696
1.280	0.0000	0.0645	0.0000	0.0645	1.300	0.0000	0.0571	0.0000	0.0571
1.320	0.0000	0.0484	0.0000	0.0484	1.340	0.0000	0.0393	0.0000	0.0393
1.360	0.0000	0.0306	0.0000	0.0306	1.380	0.0000	0.0228	0.0000	0.0228
1.400	0.0000	0.0164	0.0000	0.0164	1.420	0.0000	0.0113	0.0000	0.0113
1.440	0.0000	0.0076	0.0000	0.0076	1.460	0.0000	0.0049	0.0000	0.0049
1.480	0.0000	0.0030	0.0000	0.0030	1.500	0.0000	0.0018	0.0000	0.0018
1.520	0.0000	0.0010	0.0000	0.0010	1.540	0.0000	0.0006	0.0000	0.0006
1.560	0.0000	0.0003	0.0000	0.0003	1.580	0.0000	0.0002	0.0000	0.0002
1.600	0.0000	0.0001	0.0000	0.0001	1.620	0.0000	0.0000	0.0000	0.0000
1.640	0.0000	0.0000	0.0000	0.0000	1.660	0.0000	0.0000	0.0000	0.0000
					EXIT MOLE FRACTION	0.1163	0.4419	0.4418	1.0000

APPENDIX C

SAMPLE CALCULATIONS

Dimensionless variables and constants were used in this work in order to present the results in a more useful and general form. The relations between these variables and constants and their physical counterparts may appear somewhat obscure. A method is outlined for converting any set of physical data to its dimensionless form.

The dimensionless constants and variables are given as

$$D_i^o = D_i/(R_o L),$$

$$R_i^o = R_i/R_o,$$

$$k_1^o = k_1 L/R_o,$$

$$k_2^o = k_2 L/R_o,$$

$$X = x/L,$$

$$T = tR_o/L,$$

where R_o is some arbitrary velocity and L is the column length.

The Reduced Velocity, R_i^o

For the reaction $2A \rightleftarrows B + C$ with $R_b < R_a < R_c$, let R_o equal R_a. The velocity, R_a, can be determined experimentally from the nonreactive

chromatographic separation data by the relation,

$$R_a = \frac{L}{t_{Ra}} \tag{C-1}$$

where t_{Ra} is the peak emergence time (also commonly called the apparent retention time). The reduced velocity, R_i^o, can be calculated from chromatographic retention data as

$$R_i^o = \frac{R_i}{R_o} = \frac{(L/t_{Ri})}{(L/t_{Ra})} = \frac{t_{Ra}}{t_{Ri}} \tag{C-2}$$

Reduced Effective Diffusion Coefficient, D_i^o

For a sufficiently narrow initial square wave (or any other form of rapid injection), it can be shown that Equation (10) approaches the Gaussian distribution,

$$A(Z,T) = \frac{gA_o}{(\pi DT)^{\frac{1}{2}}} \exp(-Z^2/4DT) \tag{C-3}$$

Taking the second derivative of (C-3) with respect to Z and setting it equal to zero yields inflexion points at

$$Z^2 = 2DT \tag{C-4}$$

Equation (C-4) is commonly called the Einstein equation. The half-bandwidth, Z, at the inflexion point is called the standard deviation, σ. The bandwidth between the inflexion points is therefore two standard deviations, 2σ.

Substituting Equation (C-4) in Equation (C-3) gives the concentration at the inflexion points,

$$A(Z,T) = \frac{gA_o}{(\pi DT)^{\frac{1}{2}}} \exp(-\tfrac{1}{2})$$

The maximum concentration occurs at $Z = 0$ and is

$$A(0,T) = \frac{gA_o}{(\pi DT)^{\frac{1}{2}}} = A_{max}$$

The concentration at the inflexion points is $A_{max} \exp(-\tfrac{1}{2}) = 0.607\ A_{max}$.

Evaluating the first derivative of (C-3), taken with respect to Z at the inflexion points gives a slope of

$$\left.\frac{\partial A}{\partial Z}\right|_{Z^2 = 2DT} = A_{max} \frac{\exp(-\frac{1}{2})}{(2DT)^{\frac{1}{2}}} = A_{max} \frac{\exp(-\frac{1}{2})}{\sigma}$$

Extrapolation from the concentration at the inflexion points to zero concentration using this slope, yields a Gaussian basewidth of four standard deviations, 4σ.

In chromatographic practice, the graph of exit concentration versus time (the chromatogram) is assumed to have a Gaussian shape if the internal column concentration was Gaussian. The approximation is generally valid; but, it must be noted that even for pure Gaussian column concentrations the exit chromatogram is never exactly symmetrical. The chromatogram will always be slightly skewed toward larger times. A simple example will demonstrate the cause for this asymmetric chromatogram.

A Gaussian curve with a basewidth 4σ, is traveling through a column with a velocity of R_i cm./sec. The basewidth is given by the expression, $\sigma^2 = 2DT$. It will take $(4\sigma/R_i)$ seconds to pass a fixed point. Let the fixed point represent the column exit. On the

chromatogram, this basewidth will be

$$\Delta T_i = \frac{4\sigma}{R_i} \qquad \text{(C-5)}$$

However, the basewidth is not constant, but changing because the last material to leave the column will have diffused more than the material which has been in the column a shorter period of time. This changing basewidth gives a chromatogram skewed toward larger times. If the basewidth, ΔT_i, is small compared to the peak emergence time, t_{Ri}, the peak will be almost symmetrical and can be assumed Gaussian. For large effective diffusion coefficients or small emergence times, it must be remembered that a skewed chromatogram does not necessarily mean the column spreading is non-Gaussian.

Using Equations (C-4) and (C-5) yields

$$D_i = \frac{\sigma^2}{2t_i} = \frac{(\Delta T_i)^2 R_i^2}{32 t_i}$$

where D_i is the effective diffusion coefficient. With the relations

$$D_i^o = D_i/(R_o L)$$

$$R_i = L/t_{Ri}$$

and

$$R_o = R_a = L/t_{Ra}$$

the reduced effective diffusion coefficient can be written as

$$D_i^o = \frac{1}{32}\left(\frac{t_{Ra}}{t_{Ri}}\right)\left(\frac{\Delta T_i}{t_{Ri}}\right)^2 \qquad \text{(C-6)}$$

To calculate the reduced effective diffusion coefficient from an experimental nonreactive chromatogram, the following procedure is used:

1. Draw tangents through the exit chromatogram inflexion points (located at 0.607 times the peak maximum) to determine the basewidth, ΔT_i.

2. The apparent retention time, t_i, is measured on the chromatogram from the injection time to the peak maximum.

3. Using Equation (C-6) and the apparent retention time for component A, the reduced effective diffusion coefficient is calculated.

Other relations derived from the properties of the Gaussian equation which express the effective diffusion as some function of the bandwidth measured at various heights may be used in place of the above procedure.

The concept of theoretical plates (or transfers) has been carried over into chromatography from the theory of distillation. A good performance index for any column is the height equivalent to a theoretical plate, H, written as

$$H = \frac{L}{N}$$

where N is the number of theoretical plates. It can be shown that

$$H = \frac{\sigma^2}{L}$$

Using the Einstein Equation (C-4) gives

$$H = \frac{2DT}{L} = \frac{\sigma^2}{L} \qquad (C\text{-}7)$$

where D is the effective diffusion coefficient.

Chromatographic rate theories have been developed (32,33,34)

which explain the various contributions to the theoretical plate height. The basic approach is statistical and uses the theorem that the total variance of a group of independent statistical processes occurring simultaneously is the sum of the individual variances. The variance is the square of the standard deviation. The general approach of van Deemter et al. (34) predicts contributions to the plate height from longitudinal gas diffusion, eddy diffusion (caused by column packing), and resistance to mass transfer between and in the gas and liquid or solid phases. The dependence of the theoretical plate height on its various spreading processes can be obtained from the equation developed by van Deemter et al. While it probably cannot be used to quantitatively predict the theoretical plate height and therefore the effective diffusion coefficient, the equation offers a good guide to methods of constructing an efficient column or improving an existing column.

It is important to remember that the diffusion constant used in the mathematical description of the chromatographic reactor includes other effects in addition to longitudinal diffusion.

Reduced Reaction Rate Constants

The reduced reaction rate constant for component i is

$$k_i^o = k_i \left(\frac{L}{R_o}\right)$$

Letting

$$R_o = R_a = \frac{L}{t_{Ra}}$$

the reduced rate constant is

$$k_i^o = k_i t_{Ra} \tag{C-8}$$

Reaction Rate Constants from Experimental Data

For the batch reaction $2A \rightleftarrows B + C$, with forward and reverse reaction rates constants given as k_1 and k_2, respectively, the following equation can be written:

$$\frac{dA}{dt} = 2(-k_1 A^2 + k_2 BC) \tag{C-9}$$

For an initial equal molar mixture of B and C, the initial concentrations are $A(0) = 0$ and $B(0) = C(0) = B_o$. Noting that $B(t) = C(t)$, an overall material balance ban be written.

$$A + B + C = A + 2B = 2B_o$$

Using the material balance, Equation (C-9) reduces to

$$\frac{dA}{dt} = \frac{k_2}{2}\left[(1 - 4K_e)A^2 - 4B_o A + 4B_o^2\right] \tag{C-10}$$

where $K_e = k_1/k_2$.

When equilibrium is established, Equation (C-10) gives the equilibrium concentration of A as

$$A_e = \frac{2B_o}{1 + 2(K_e)^{\frac{1}{2}}} \tag{C-11}$$

Integrating Equation (C-9) to determine the time necessary for half conversion of the reactants gives

$$\int_0^{A_e/2} \frac{dA}{(1-4K_e)A^2 - 4B_o A + 4B_o^2} = \int_0^{t_{\frac{1}{2}}} \frac{k_2 dt}{2} \tag{C-12}$$

An expression for the reverse reaction rate constant, k_2, as a function of the reaction half time can be obtained by evaluating the integrals in Equation (C-12) with the aid of Equation (C-11).

$$k_2 = \frac{1}{4B_o(K_e)^{\frac{1}{2}}(t\frac{1}{2})} \ln \left[\frac{1 + 6(K_e)^{\frac{1}{2}}}{1 + 2(K_e)^{\frac{1}{2}}}\right] \qquad \text{(C-13)}$$

Kummer and Emmett (30) studied the reaction of equal molar mixtures of hydrogen and deuterium. For this reaction at 77.4° K., the authors gave a time for half conversion of 3-10 seconds over a singly-promoted iron catalyst. Woolley et al. (31) gave an equilibrium constant of 1.90 for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ at 77.4° K. This value is the reciprocal of the equilibrium constant for the reaction written in the other direction. Assuming the initial concentration, B_o equal to $\frac{1}{2}$, Equation (C-11) gives the equilibrium concentration, A_e, as 0.408.

With the data of Emmett (30), Equation (C-13) gives

$$0.054 \leq k_2 \leq 0.18$$

and

$$0.028 \leq k_1 \leq 0.095$$

If an average value of 6.5 seconds for the half conversion time is used, the calculated forward and reverse reaction rate constants are

$$k_1 = 0.044$$

and

$$k_2 = 0.083$$

where the rate constant units are $(\text{mole/l.})^{-1}$ $(\text{sec.})^{-1}$.

Equations (C-2), (C-6) and (C-8) can be used to calculate the reduced variables for component velocities, effective diffusion coefficients, and the reaction rate constants from nonreactive chromatographic and reaction kinetic data.

Although the data for the velocities and diffusion coefficients must be from nonreactive experiments, this requirement does not preclude the use of actual data from a chromatographic reactor. To insure the conditions used for developing the equations, no reaction should occur during passage of the component through the column when velocities and diffusion coefficients are being measured. Otherwise the apparent retention time and the peak basewidth would not be related directly to the component velocity and effective diffusion coefficient.

Data obtained on a chromatographic reactor by injecting separate samples of each of the reaction products in the column at different times can be used to calculate the reduced constants. No reaction can occur because the products are separated. Therefore, the velocities and diffusion coefficients of the products can be calculated. The reactant values can be estimated from an average of the values of the products, from the known separation ratio for the chromatographic packing, or from the chromatographic reactor exit concentration during a reaction run, ignoring the errors of using reactive data.

A simple method for obtaining the necessary data is to construct a column identical to the chromatographic reactor, but without a

reaction catalyst. All the reduced constants for the reactants and products can be calculated from one chromatographic analysis. The assumption implicit in this scheme is that the only change on addition of a reaction catalyst is that of promoting the desired reaction.

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